SOLUBILITY
in the
VAPOUR PHASE.

BINARY LIQUID SYSTEMS
and the
MIXTURE RULE.

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by

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I have to record my great indebtedness to Dr. Wright for the interest he has taken in the work and for his most valuable guidance and advice throughout the period of this research.

A binary solution may be regarded as something between a compound and a simple mixture of its two constituents.

The physical properties of a solution cannot as a rule be calculated from those of its constituents, and the influence exerted by each constituent on the properties of the other has been designated by the term "solvent effect".

Solvent effect is small if the two constituents are closely related chemically, for example, if they are the neighbouring members of an homologous series. On the other hand it may have a high value if the solution constituents differ greatly in chemical nature, as is the case for an aqueous solution of sulphuric acid.

In gaseous mixtures at atmospheric pressure the molecules are so widely separated that any interaction between them is slight, and therefore as a rule solvent effect is small; but as is shown in the first part of this thesis, it need not be altogether absent.

In the case of liquid solutions, numerous investigations as to the extent and nature of solvent effect have been carried out. The second part of the thesis deals with an attempt to decide which of the three methods -mass, volume or molecular proportions-, is the most suitable for expressing the composition of a liquid solution when investigating the solvent in such liquid systems.

SOLUBILITY

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An account of this work has been accepted by the Journal of the Chemical Society for publication.

The mutual nature of solubility with regard to the two constituents of a solution is clearly seen when both solute and solvent are liquids. Benzene is only slightly soluble in water and water is slightly soluble in benzene; when the constituents are phenol and water the solubility of each substance in the other is much greater, but the two solubilities are still approximately of the same magnitude. We do not find one liquid A extremely soluble in a second liquid B, whilst B is only slightly soluble in A.

When one constituent of the solution is a solid and the other a liquid, the mutual nature of solubility is not evident, since the liquid cannot with ease diffuse into the solid, and further, solid solutions of high concentration can only be produced when the two constituents have a similar crystalline nature. In such cases the mutual nature of solubility becomes evident when the solid is melted; thus solid benzoic acid is slightly soluble in water and water is slightly soluble in molten benzoic acid, as is shown by the lower melting point of that substance when heated under water.

But in the case of solutions of gases in liquids, both constituents are found in the two phases, and it becomes of interest to determine if the system shows a mutual solubility between the components such as is found for a liquid pair. For example, will a gas,

such as ammonia or hydrochloric acid which is very soluble in water, attract an excess of water into the vapour phase? In other words, will there be an attraction between the two substances in the gaseous as well as in the liquid state?

There is no recorded case of a liquid being more volatile in the presence of a gas than when it exists alone. An extensive investigation of the partial pressures of aqueous ammonia solutions (Perman, J. C. S. 83, 1903, 1168) showed that although ammonia is very soluble in water, still there is a smaller concentration of water vapour in the gas phase, when that liquid is confined by an atmosphere of ammonia, than when the water is allowed to evaporate into a vacuous space. However, this lowering of the saturated vapour pressure of a liquid in the presence of a soluble gas may be attributed to the ordinary lowering of the vapour pressure caused by a solute, so that the concentration of the liquid vapour in the gas phase is less than when the gas is absent.

Nevertheless, the fact that the gas does dissolve in the liquid is evidence that there is an attraction between the molecules of the two substances and it seems to be reasonable to expect that this attraction will exist in the gaseous as well as in the liquid phase. If it is assumed that such an attraction does exist in the gaseous phase, then the total gas pressure will be less than the sum of the partial pressures of the two constituents, vapour and gas, when considered separately and this difference

between the total pressure and the sum of the partial pressures enables the existence of the attraction to be detected. However, since there are two factors tending to lower the vapour pressure of the vapour when liquid is present, firstly the attraction between the constituents in the gas phase and secondly, the lowering produced by a solute in the liquid, it is necessary to eliminate the second one before the first one, the attraction, can be examined at all. When the conditions are such that the liquid is completely vapourised, then the second factor disappears, so that an examination of the partial and total pressure when an unsaturated vapour is mixed with a gas, should afford information as to the existence and amount of any attraction between the molecules in the gaseous phase.

It has been stated above that solubility of the gas in the liquid shows the existence of attraction between the molecules, and therefore the attraction might be expected in the vapour as well as in the liquid phase. Further, it might be argued that the greater the solubility of the gas in the liquid, the greater will be the attraction between the molecules in the vapour phase, so that the more soluble gases in the liquids should give greater lowerings of the gas pressure.

With this in view, it was decided to investigate this attraction by examining the unsaturated vapour pressures of certain volatile liquids in certain

gases with which they presumably do not interact chemically. An account of the work carried out is given in the following paper. A suitable apparatus and method having been adopted, the unsaturated vapour pressures of definite quantities of liquid were measured and compared, where possible, with the solubilities of the gases in the liquids.

Historical

Before giving details of the method used and the results obtained, it is interesting to consider the facts observed by other investigators, because they indicate that the vapour pressure does vary according to the gas into which the liquid is evaporating. In many cases it has been noted that the saturated vapour pressures of some liquids in a gas (usually CO_2, H_2, or air) were less than the saturated vapour pressures of the liquids in vacuo. In practically every case there was liquid present during the determination of the vapour pressure so that it is possible to explain the lowering by solution of the gas in the liquid, although the various authors themselves put forward different explanations. At the same time, the possibility cannot be ignored that mutual attraction between the molecules in the gas phase might be responsible for part of the lowering. Therefore, although these investigations where liquid is present and the gas is

saturated with vapour, are of little value as evidence of the existence of attraction between the molecules in the vapour phase, they do show that the vapour pressure is influenced in some way by the gas into which the liquid is evaporating.

The first person to observe this difference between the saturated vapour pressure in vacuo and in a gas, and to make a special investigation into the cause, was Regnault. A full account of his work is given in the Ann. Phys. Chim. 1845, 3, 15, 129, and the Mem. Acad. Sci., 1862, 26, 679,. The first method he used was a dynamic one, in which a known volume of air or nitrogen was drawn through wet sponge or moist silk screens, thus saturating the gases with water vapour. The water carried over was absorbed in sulphuric acid and its weight determined He found that the pressures calculated from the weights of water in known volumes of saturated air and nitrogen were invariably 1-2% lower than those developed in vacuo. He believed that the differences might be due to a constant error in his apparatus or procedure, but he says, "Mes efforts pour determiner la cause d'une erreur de cette description ont été sans résultat",(Ann. p. 137). At first he thought that the mercury in his apparatus was removing a little of the oxygen from the air, but when he repeated the experiment with nitrogen in place of air, he found the same lowering. He then extended the investigation to other liquids using two statical methods.

In one of them, he broke a small bulb containing the liquid whose vapour pressure he wished to determine inside a flask to which a mercury manometer was attached. The liquids examined were ether, carbon disulphide and benzene; the gas in every case being air. Again the pressures in air were lower than those obtained in the absence of air. With ether the differences varied from 1-2.9%, with benzene 2.9-4.8%, and with carbon disulphide between 0.8 and 1.2%. (It should be noted that benzene is a much better solvent for these gases than carbon disulphide).

To test the matter thoroughly, he went ahead with the next method, because he could not rid himself of the idea that there might be some experimental error occurring in his methods. He introduced small quantities of ether into a graduated tube containing either air, hydrogen or carbon dioxide. The gas pressure, corresponding to each volume being known at a constant temperature, a measurement of the total pressure after each successive decrease of volume gave the partial pressure of the ether vapour. He found that, even when the ether was condensing on the walls of the tube, the vapour pressures of the ether in the air or hydrogen were still less than that of the ether in vacuo, and only approached nearer and nearer to the value in vacuo when the pressure of the air or hydrogen was gradually increased to about 1200mm. At this pressure the values were actually very slightly in excess of the value found in vacuo. In the case of carbon dioxide

however, even when the pressure of the gas was raised to about 1300mm. the vapour pressure of the ether never rose higher than 245mm., compared with a value of 260mm. for the vapour pressure of ether in vacuo. (Mem.Ac.Sc. 1862, pp. 691-693).

Regnault's ultimate explanation of the lowering was that it was due to the molecular attraction between the material of the walls of the flask and the vapour particles causing condensation of the liquid. Then equilibrium between the liquid and the vapour was never reached because the presence of the gas slowed down evaporation of the liquid and a film of liquid of sufficient thickness to saturate the walls was never formed, because the liquid ran down the walls under the force of gravity. (Mem. p. 694).

Shaw in a Study of Hygrometric Methods (Phil. Trans., 1888, 179, 73) noted Regnault's results with water and repeated them using a modified method of Regnault's original dynamical one. His results also showed slight differences from the calculated values, in the same direction as Regnault's.

Linnebarger (J.A.C.S., 1895, 17, 615, and Chem. News, 1895, 72. 167) in an investigation of the saturated vapour tensions of mixtures of volatile liquids measured the saturated vapour tensions of a number of the pure liquids and found that several of them were lower than those obtained by other investigators using different

methods. His own method was a modification of Regnault's in which air was drawn through the apparatus. He found that the greatest lowering was obtained with the liquids of greatest volatility; the less volatile liquids gave results perfectly concordant with those obtained by others. He attributed the differences to the volatility of the liquids but Campbell (see below) points out that the differences increase with the solvent power of the liquids for the gases.

Campbell (Trans. Faraday Soc.. 10, 1914, 197) in a paper which contains references to the various methods employed by different investigators to determine the saturated vapour pressures of liquids, describes an apparatus of his own design, which he used to investigate the effect of a gas on a liquid evaporating into it. The principle of the method is that of allowing a liquid previously saturated with hydrogen at a definite temperature to evaporate into a space containing the same gas under the same conditions. In his preliminary experiments he determined the saturated vapour pressures of various liquids when allowed to evaporate into air and in all cases, the results, although concordant, were lower than those obtained by other methods. Carbon dioxide, a more soluble gas, and hydrogen, a less soluble one, were substituted for air, and lowerings were also obtained. The deviations from the value in vacuo were greatest in the carbon dioxide and least in the hydrogen.

A summary of Campbell's results is given below, and for the sake of comparison, the values obtained by other investigators are given in the last three columns. From an examination of the figures, it will be noted that the lowering is considerable. In the case of chloroform in carbon dioxide, the value found is only about two-thirds that of the value in the absence of gas. With methyl alcohol in carbon dioxide, the value is about three-quarters that in vacuo.

		Vapour pressure in presence of			Vapour pressure of liquid		
Liquid	Temp.	CO_2	Air	H_2	vapour alone.		
Ether	30°C	530mm.	605mm.	642.1mm.	634.8(a)	647.9(b)	648.2(c)
CS_2	30°	402..	425..	431.9..	432.8(c)	434.6(ab)	437.0(b)
$CHCl_3$	30°	169..	238..	243.6(N_2)	-	247.5(a)	245.9(b)
CH_3OH	40°	191..	250.5.	257.4..	243.5(a)	259.4(d)	260.5(b)
C_2H_5OH	60°	-	344.3.	347.3..	350.2(ab)	352.1(e)	-
H_2O	70°	-	225.8.	230.8..	233.8(a)	-	-

The figures in the last three columns are taken from Landolt-Bornsteins-Meyerhoffer's Tabellen and Castell Evan's Physico-Chemical Tables.

a) Regnault, (Mem.Acad.Sc.,1862. 26, 339).
b) Ramsay & Young, (Phil.Trans.,1886, 177, 1,123
1887, 178, A, 57).
c) Batteli.
d) Dittmar & Fawsitt, (Edin.Trans.,1886-87,23 ,509).
e) Schmidt, (Zeit.phys.Chem.,1891, 8, 628).

No value for Chloroform in hydrogen is given because most irregular results were obtained.

Campbell's explanation of the differences obtained, is that gases are adsorbed on liquid surfaces just as they are on solid surfaces. In support of this, he draws attention to the fact that CO_2 is the most soluble and is adsorbed to the greatest extent by solids, notably charcoal, and that H_2, the furthest removed from its critical temperature is least soluble and least easily adsorbed by charcoal. The order is the same when the gases are arranged according to the magnitude of the vapour pressure lowering which they cause. Campbell also tries to explain Regnault's results in this way.

He points out also, that the total lowering cannot be due to the solution of the gas in the liquid. He calculates from figures given by Just, (Zeit.phys.Chem.,1901, 37, 342), that the quantity of dissolved H_2 in ethyl alcohol is only sufficient to lower the vapour pressure of the alcohol by 0.08%, while the actual lowering at 60°C is 0.82%.

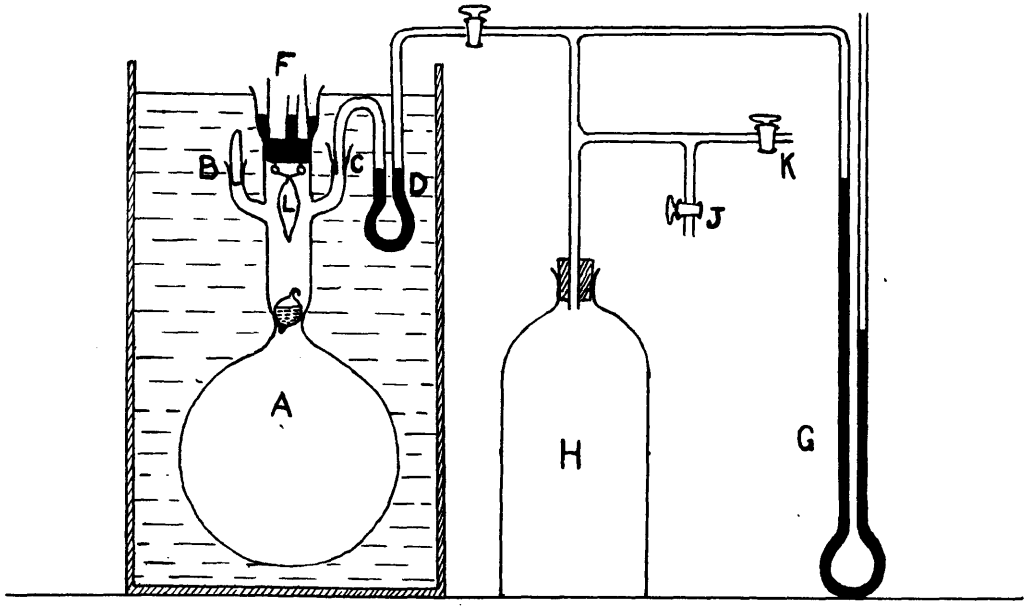
Up to this point the experiments referred to have only shown that the vapour pressure is influenced by the gas into which the liquid is evaporating and from the point of view of this investigation, the presence of liquid renders them of comparatively little value, because of the lowering, unknown in extent, produced by the solution of the gas in excess liquid, and it is not known whether the lowering is to be wholly attributed to the solution of the gas in the liquid or whether attraction in the vapour state plays a part.

The much more important case where no liquid is present has now to be considered. Masson and Dolley (Proc. Roy. Soc., A103, 1923, 524), have found a decrease in pressure of about 8% when equal volumes of ethylene and argon or ethylene and oxygen are mixed at 100 atmospheres pressure, thus affording definite evidence of attraction between the gas molecules at high pressures.

The next paper by Sayce and Briscoe (J.C.S. 1929, 1302) contains the first description of a method in which liquid is absent and in which both the concentration and partial pressure of a vapour are measured independently in the presence and also in the absence of gas. The authors point out that, up to that time, there is no recorded case of the precise measurement simultaneously of the pressure and the concentration of a vapour. They were endeavouring to test the validity of Campbell's statement, that the low values obtained by himself and others were due to the adsorption of gas at the liquid-gas interface. If there is no liquid present, then there is no liquid-gas interface and the vapour pressure of the liquid cannot be affected, as Campbell suggests. From their results Sayce and Briscoe definitely contradict the view that the diminution of the vapour pressure (saturated) of a liquid in presence of a gas can be wholly attributed to the effects of solution or adsorption in the liquid.

They did not extend their investigation beyond finding the vapour pressures of ether and pentane

in vacuo and in carbon dioxide, because of experimental difficulties, but on consideration it seemed possible that a simplified model of their apparatus might be constructed, which would give results a little more readily, without affecting the accuracy to any great extent. In consequence of this, their apparatus and method are described below in some detail.



In the diagram, A is a large flask of 1200cc. capacity with a constriction in the neck at E. The stopper in the flask carries two sealed-in platinum wire loops from which a chisel-ended glass hammer L is suspended by a bridge of fuse wire. D is an isoteniscope connected to a manometer and to a large vessel H. The pressure in H can be regulated by evacuation at J or admission of air at K, so that the mercury levels in D can be readily adjusted and the pressure

in A found from the manometer G. The sidearm B is used for evacuation or introduction of gas. In the actual experiment a thin walled bulb of 3-10cc. capacity was filled with ether or pentane, weighed and placed at E, and a current of electricity passed through the fuse wire, causing the hammer to fall and break the bulb. The pressure exerted by the liquid vaporising was then read off on the manometer G, after the levels in the isoteniscope had been adjusted. The readings were only taken after diffusion was complete and the readings constant.

Their results show that there was a definite lowering of the unsaturated vapour pressure in the presence of carbon dioxide at a pressure of approximately 50cm. mercury.

Ether in Vacuo.					
Volume of flask.	Initial Pressure.	Final Pressure.	Vapour Pressure.	Weight of vapour.	Vapour pressure of 1gm. vapour per litre.
1208.3cc.	1.82mm.	44.87mm.	43.05mm.	.20374gm.	255.3mm.
1208.47..	.31..	243.39..	243.08..	1.18576..	247.7..
Ether in carbon dioxide.					
1208.89	494.24..	537.07..	42.83..	.20552..	251.9..
1208.36	499.81..	710.46..	210.65..	1.04588..	243.4..
1208.48	497.21..	757.19..	259.98..	1.29962..	241.8..

These figures also show the effects of adsorption of ether by the walls of the flask, since the unsaturated vapour pressure exerted by 1gm. of vapour in 1 litre of space diminishes progressively, as the actual

concentration of the vapour increases.

In the case of pentane, there was a grave irregularity in the results which is difficult to understand, although the lowering of the unsaturated vapour pressure of pentane in carbon dioxide appears to be distinctly greater than the corresponding lowering of the vapour pressure of ether. Sayce and Briscoe themselves describe the method as so laborious as to be unsuitable for the investigation of a large number of cases. For one thing, the glass hammer could not always be relied upon to stop at the indentations in the neck of the flask and if it did not, the destruction of the flask, as well as the bulb, was the result. Again, because of the large capacity of the flask, it had to be left in the thermostat for 8-10 hours before the readings could be taken as constant. In consequence, they contented themselves with the investigation of the vapour pressures of ether and pentane in vacuo and in a single gas, carbon dioxide, as already stated.

Experimental

In the introduction it was stated that the object of this investigation was to examine the vapour pressures of certain volatile liquids in the presence of certain gases, and so discover if there is any attraction between the molecules of the vapour and the gas into which the liquid is evaporating, and if there is, to compare the attraction with the solubility of the gas in the liquid.

In the pages that follow, an account is given of the work carried out, when the unsaturated vapour pressures of methyl alcohol, acetone, ether and chloroform were measured in air, CO_2, HCl, NH_3 or SO_2. In the majority of cases studied by other investigators, the gases were air, H_2 and CO_2 which are on the whole, less soluble in the liquids mentioned than NH_3, SO_2 or HCl. Therefore it was thought that it would not be surprising to find that these gases give a greater lowering of the vapour pressures than the former. Some preliminary experiments bore this out.

In these experiments, measurements more of a qualitative nature were made using a different method from that to be described later. Equal volumes of a gas (CO_2, SO_2, NH_3 or HCl) and air saturated with methyl alcohol vapour were mixed together and left to come to equilibrium and then the decrease in pressure at constant volume was measured; the results being shown in Table I. They indicate that there is a strong attraction between the HCl and methyl alcohol, which is much greater than the attraction between the vapour and the other gases; which is not unexpected since HCl is the most soluble in liquid methyl alcohol.

Table I.

Contraction in mms. of Hg. when air is saturated with methyl alcohol vapour and is mixed with an equal volume of a second gas at 25°C.

HCl.	CO_2.	SO_2.	NH_3.
59mm.	1mm.	7mm.	8mm.
ol..	2..	8..	9..

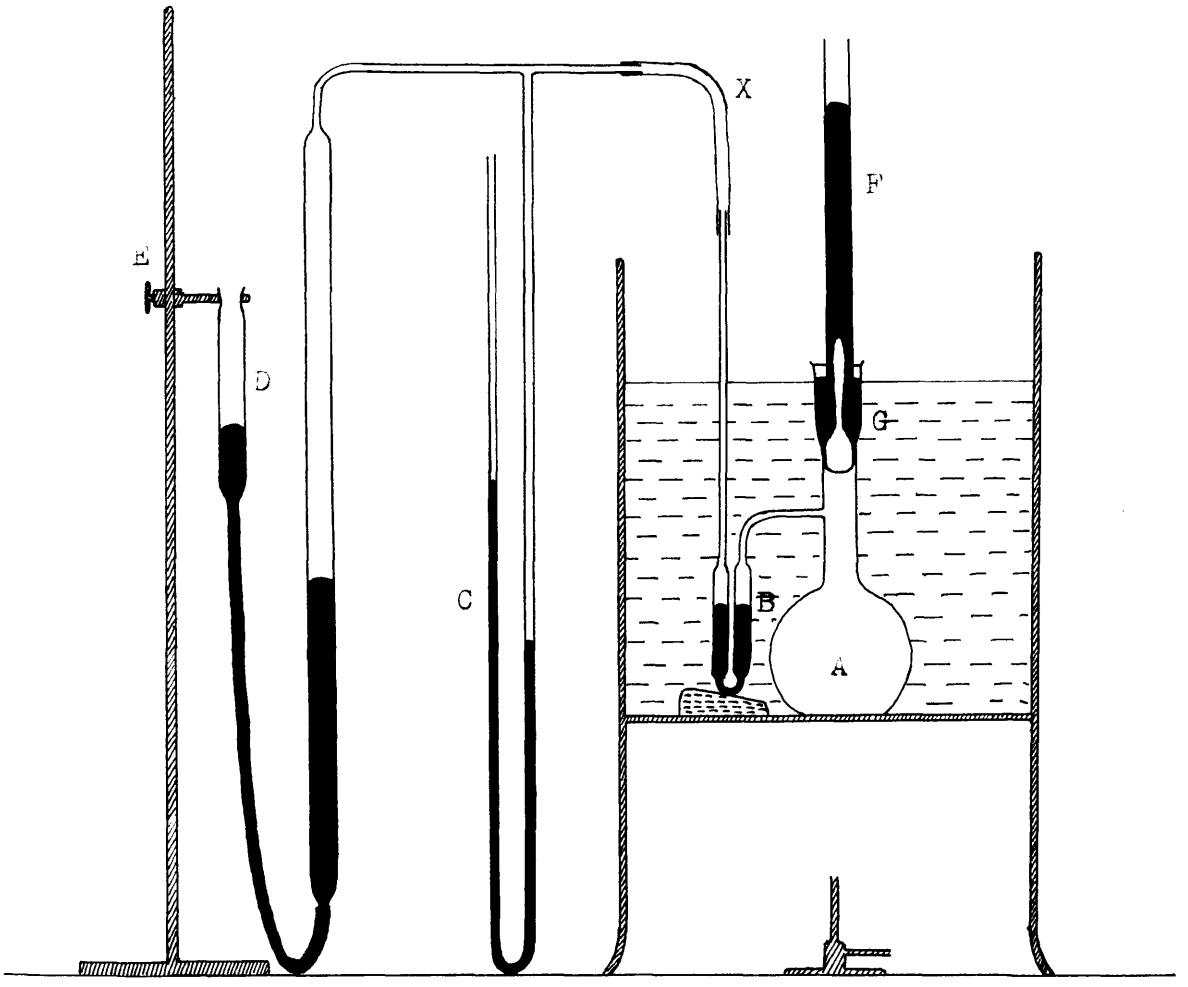
No great stress must be placed upon these figures because, besides the vapour and the gas, there is always air present, making three constituents in the vapour phase. They can only be taken to show that the effect is there, and that the HCl appears to have a much greater effect than the other gases.

Nevertheless, when they are considered along with the lowering of the vapour pressure of ether in the presence of CO_2 observed by Sayce and Briscoe, there is evidence that the attraction between the molecules does exist, so it seemed profitable to pursue the investigation further, using a method which would give accurate quantitative results. In the end, the apparatus described below, a simplified model of Sayce and Briscoe's was constructed.

Apparatus

In Fig. II on page 17, A is a flask of about 250c.c.s capacity, with a sidearm constructed in the form of a U tube; the limbs of which are made of tubing of at least 1cm. diameter, which is the minimum diameter for manometers recommended by Travers (Study of Gases). On the U tube a mark is etched at B.

The flask has a specially constructed neck G, as shown, and is closed by a ground glass stopper. The neck is made in this fashion for two reasons, the first being that it allows a long glass tube F to be fixed above



(Fig. II)

the glass stopper. When this tube is filled with mercury to a height of about 20cm., it acts as a very efficient seal and also prevents the stopper from being blown out with increase of pressure inside the flask. (The second reason will be given later.)

C is an ordinary manometer which is used

to find the pressure inside the flask A, the readings being taken by means of a cathetometer, not shown in the diagram. D is a reservoir of mercury on an iron stand with a rack and pinion E, by which it can be slowly raised or lowered, thus altering the pressure inside the apparatus. By this means the level of the mercury in the U tube or isoteniscope can be altered and adjusted. The flask and U tube are kept at 25°C in a thermostat fitted with a mechanical stirrer and a thermoregulator. These are the bare details of the apparatus.

To explain how the experiments were carried out, it is proposed to describe in detail one actual determination, that of the vapour pressure of ether in carbon dioxide.

Method

The volume of the flask A, as far as the etched mark B, is determined by weighing the flask several times with water. The flask is carefully dried and then with the glass stopper removed, but closed instead by a rubber stopper fitted with a calcium chloride tube, (see p.23 Fig.111,b,) it is placed in the thermostat. A lead jacket is placed around the flask to keep it submerged and the limbs of the U tube carefully adjusted, using a plumb line, so that they are always vertical. Then 15cc. of mercury are poured into the flask to lie in the bottom and so break the fall of the Hoffmann bottle when it is introduced.

Carbon dioxide is passed for five minutes or so, through the limbs of the U tube into the flask and out through the calcium chloride tube, which ensures that no air is left in the sidearm. The U tube is then filled with mercury up to the etched mark; the calcium chloride tube and stopper are removed and a rubber stopper carrying an inlet and an outlet tube are inserted in their place. (p. 23, Fig. III, c.) The inlet tube extends to the bottom of the flask, while the outlet one just goes through the stopper. Carbon dioxide is passed through this inlet tube for 15-20 minutes, the rubber stopper is removed and the calcium chloride reinserted. (When not in use, this calcium chloride tube is kept carefully closed, so that it contains only carbon dioxide when it is inserted at this point.) To allow the carbon dioxide to take on the temperature of the bath, the apparatus is left for 25-30 minutes.

Meanwhile a tiny Hoffmann bottle which holds about 0·07'35gm. ether is carefully weighed and filled with ether. (see Note below.) The calcium chloride tube is removed, the Hoffmann bottle is dropped in and the glass stopper rapidly but carefully inserted, after which the long glass tube is placed in position and filled with mercury. The reservoir of mercury is raised to the top of the iron stand, the flask is connected to the manometer by rubber tubing at X, and the reservoir is lowered. By this means, a diminution of pressure of 20cm. can be obtained in the flask A. (For this reason the upper part of one limb

of the U tube is made much longer and narrower than the lower part which forms one limb of the isoteniscope). Then the temperature of the thermostat is raised rapidly to about 75°C by adding hot water, a temperature, which combined with the reduction in pressure causes the ether to evaporate rapidly. The flask is kept at this temperature and reduced pressure for an hour, then it is brought back to 25°C and the pressure restored to normal, by suitably moving the reservoir of mercury.

After two hours the first reading is taken. The reservoir is now adjusted until the two levels in the isoteniscope are the same when viewed against the horizontal wire in the telescope of the cathetometer. The difference in levels of the mercury in the manometer, corrected for any change in the atmospheric pressure during the course of the experiment, gives the pressure exerted by the ether vapour in the flask in the presence of carbon dioxide.

The readings are continued over a period of 2-2½ hours, at intervals of 15 minutes, to ensure that the pressure is constant.

In the Table below, the actual figures for one estimation of the vapour pressure of ether in carbon dioxide are given. Column IV gives the pressure recorded on the manometer, while V gives the pressure corrected for changes in the barometric pressure. With regard to column II it may be remarked that no readings were taken in any

determination until at least three hours had elapsed since the commencement of the experiment.

Table II

Weight of ether.	Time of reading	Barometric pressure	Increase in pressure	Corrected pressure	Average
0.0738gm.	10-15am.	756.55mm.	-	-	
	1-30pm.	758.40..	74.72mm.	76,57mm.	
	1-45..	758.45..	74.65..	76.50..	
	2-0 ..	758.50..	74.52..	76.42..	
	2-15..	758.60..	74.40..	76.40..	
	2-30..	758.60..	74.45..	76.45..	76.41mm.
	2-45..	758.65..	74.15..	76.20..	
	3-0 ..	758,70..	74.17..	76.2?..	
	3-15..	759.10..	73.87..	76.42..	
	3-30..	759.20..	73.87..	76.52..	

The procedure described was decided upon only after several trials and observations, about which it is necessary to say a few words.

Notes on the apparatus and method.

1) The apparatus was inferior to Sayce and Briscoe's in that it was impossible by means of it to determine the vapour pressure of a liquid in vacuo. As a result, the best that could be done was to compare the vapour pressure in the gases with the pressure found in air. On the other hand, each determination could be carried out with greater ease in less time and with less chance of damage.

Sayce and Briscoe advocate that when gas is present in the flask as well as vapour, no readings should be taken until 8-10 hours (3-4 in vacuo) have elapsed, but in the preliminary experiments of this series, made with ether in air, readings were taken at intervals over periods of 6-7 hours and in some cases, 24 and even 72 hours after the ether had been introduced into the flask, and it was found that the readings were constant approximately 3 hours after the commencement of the experiment. In this case the smaller flask (250cc.) hastened the attainment of equilibrium.

11) Weighing of Ether. In the first experiments the ether was not weighed, but an attempt was made to introduce a definite quantity each time. The Hoffmann bottle was filled with ether and placed inside a boiling tube in the thermostat. Excess ether was placed in the bottom of the tube, thus saturating the air inside the tube with ether vapour, and as a result evaporation from the Hoffmann bottle was practically nil, while it was coming to the temperature of the bath. Then it was removed quickly and immediately dropped into the flask. Thus the same quantity of ether was supposed to be obtained each time, but on examination this was found not to be the case. The vapour pressures of the ether in air alone did not agree amongst themselves; neither did those of ether in carbon dioxide, although there was a distinct difference between the two sets of readings, and therefore it was decided to

try another method.

The Hoffmann bottle filled with ether was weighed on the balance and the weights were left on the pan while the Hoffmann was filled up again with ether. Then it was placed back on the pan of the balance which was allowed to swing until, by evaporation of a tiny quantity of ether from the stopper, the bottle balanced the weights, when it was immediately removed and dropped into the flask.

One could not be completely satisfied as to the accuracy of this method because of the volatility of the ether, but the results obtained by it were more concordant than those obtained by the first method. (see Table IIa,-Vapour pressure of ether.) The other liquids used, methyl alcohol, acetone,and chloroform did not offer the same difficulty in weighing, because of their lower volatility.

III) In the section above dealing with the description of the apparatus, reference is made to there being two reasons for the neck being constructed as in Fig. III, (a), the second reason being omitted at the time.

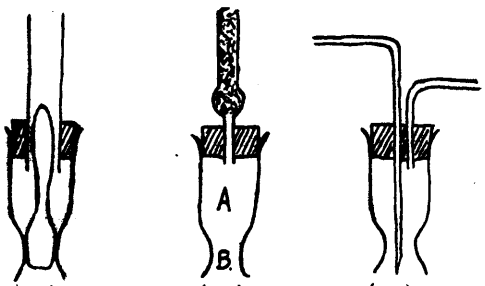


Fig. III.

It was thought that with an ordinary neck, as was tried in the preliminary experiments, the removal of a stopper of any kind, to introduce the

Hoffmann bottle, allowed the possibility of air getting into the flask and displacing some of the gas. With this design however, the space A Fig.III (b) above the ground glass surface B is also filled with gas and so, when the Hoffmann bottle is introduced, there is much less chance of air getting into the flask.

IV) In order to test if all the air was being driven out of the flask by the different gases, water was added to the flask at the end of each experiment, when the gas was ammonia, hydrochloric acid or sulphur dioxide, to dissolve the gas, so that the quantity of gas present could be determined by titration against standard acid or alkali. The quantity of gas present was then compared with the quantity that theoretically filled the flask, a quantity which could be readily calculated, thus affording a check on the efficiency of the method of filling the flask with gas. Even without this theoretical value, if the titrations were constant for any one gas, it could be assumed that the flask was completely filled with the gas in question. In actual practice, the latter course was usually adopted.

V) The four liquids used were obtained from British Drug Houses and were of A.R. quality. Ammonia and sulphur dioxide were obtained from cylinders. The ammonia was washed by bubbling it through a saturated solution of

ammonia and dried by passing it through soda lime. The sulphur dioxide was passed through concentrated sulphuric acid to remove any moisture. Carbon dioxide was prepared from marble chips and HCl, passed through a solution of sodium bicarbonate and through sulphuric acid finally to dry the gas. The HCl gas was obtained from ammonium chloride and sulphuric acid.

Results.

The results obtained are tabulated below in Tables IIa, b, c, and d,

The first column gives the weight of liquid used; the second one the pressure in mm., exerted by that weight of liquid in the flask, and the third is a figure obtained by calculation. In order to compare the vapour pressures exerted by different weights of liquids, it is necessary to reduce the figures to some common basis and it was decided to express each vapour pressure as the pressure exerted by a millimol of the liquid in a volume of 1000cc. at 25C.

Thus, using the figures given on page 21, 0.0738gm. ether had a vapour pressure of 76.41mm.

The volume of the flask was 254.8cc., but from this there must be subtracted 15cc., the volume of mercury added to the flask and also 0.26cc., the volume

occupied by the glass of the Hoffmann bottle.

Final volume = 239.54cc.

0.0738gm. ether exerts a pressure of 76.41mm. in 239.54cc.

1 millimol .. .. ? .. .1000cc.

$$= \frac{76.41}{} \times \frac{239.54}{1000} \times \frac{0.074}{0.0738} = 18.35\text{mm.}$$

Then since 1 gram molecule occupies 22400cc. at 760mm. and 0°C, 1 gram molecule has a pressure of 760mm. in a volume of 22400cc. at 0°C.

From this 1 millimol exerts a pressure of 18.58mm. in a volume of 1000cc. and at a temperature of 25°C.

This is the theoretical value, 18.58mm.

Table IIa.

Vapour Pressure of Ether at 25°C.

	Weight of Ether taken	Actual Pressure measured.	Calculated Pressure.	Average.
Air.	0.0739gm. 0.0738.. 0.0737..	78.45mm. 78.45.. 78.14..	18.82mm. 18.84.. 18.79..	18.82mm.
CO_2	0.0737.. 0.0738.. 0.0738..	76.31.. 76.19.. 76.41..	18.35.. 18.30.. 18.35..	18.33..
SO_2	0.0735.. 0.0737.. 0.0738..	72.01.. 71.95.. 72.20..	17.37.. 17.30.. 17.34..	17.34..
NH_3	0.0738.. 0.0738.. 0.0739..	76.13.. 76.72.. 76.03..	18.28.. 18.43.. 18.24..	18.32..
HCl	0.0738.. 0.0738.. 0.0739..	58.88.. 58.48.. 56.82..	14.15.. 14.05.. 13.37..	13.92..

Table IIb.

Vapour Pressure of Methyl Alcohol at 25°C.

	Weight of Alcohol taken.	Actual Pressure measured.	Calculated Pressure.	Average.
Air	0.0332gm. 0.0329.. 0.0327.. 0.0328.. 0.0326..	81.95mm. 81.23.. 81.14.. 80.94.. 81.16..	18.93mm. 18.94.. 19.03.. 18.92.. 19.09..	18.98mm.
CO_2	0.0329.. 0.0330.. 0.0327.. 0.0323.. 0.0327.. 0.0326.. 0.0327.. 0.0324..	76.14.. 76.36.. 75.66.. 78.05.. 78.99.. 78.77.. 79.58.. 78.83..	17.75.. 17.74.. 17.74.. 18.54.. 18.53.. 18.54.. 18.66.. 18.66..	18.27..
SO_2	0.0328.. 0.0328.. 0.0325.. 0.0326..	75.53.. 74.51.. 74.52.. 74.97..	17.66.. 17.43.. 17.59.. 17.64..	17.58.
NH_3	0.0330.. 0.0329.. 0.0329.. 0.0330..	61.35.. 64.12.. 64.30.. 64.60..	14.27.. 14.95.. 14.99.. 15.02..	14.81..
HCl	0.0325.. 0.0325.. 0.0325.. 0.0325.. 0.0182..	-33.69.. -35.44.. -35.53.. -19.65.. -13.91..	-7.95.. -8.36.. -8.39.. -4.64.. -5.86..	-7.04..

Table IIc.

Vapour Pressure of Acetone at 25°C.

	Weight of Acetone taken.	Actual Pressure measured.	Calculated Pressure.	Average.
Air	0.0329gm. 0.0329.. 0.0329.. 0.0329..	46.24mm. 46.87.. 46.91.. 46.53..	19.54mm. 19.81.. 19.83.. 19.66..	19.71mm.
CO_2	0.0324.. 0.0330.. 0.0326.. 0.0329.. 0.0329..	45.69.. 45.15.. 45.55.. 44.94.. 45.71..	19.61.. 19.02.. 19.43.. 18.99.. 19.32..	19.27..
SO_2	0.0327.. 0.0328.. 0.0332.. 0.0328..	40.53.. 41.22.. 41.57.. 40.93..	17.24.. 17.47.. 17.41.. 17.35..	17.37..
NH_3				
HCl	0.0328.. 0.0326.. 0.0327.. 0.0326.. 0.0330..	31.31.. 28.81.. 24.08.. 23.40.. 25.02..	13.26.. 12.28.. 10.23.. 9.98.. 10.54..	11.26.

Table IId.

Vapour Pressure of Chloroform at 25°C.

	Weight of Chloroform taken	Actual Pressure measured.	Calculated Pressure.	Average.
Air.	0.0627gm. 0.0627.. 0.0625.. 0.0621..	42.11mm. 42.34.. 41.53.. 41.40..	19.23mm. 19.32.. 19.01.. 19.08..	19.16mm.
CO_2	0.0624.. 0.0626.. 0.0620.. 0.0619..	40.96.. 40.70.. 40.56.. 40.71..	18.82.. 18.61.. 18.74.. 18.82..	18.75..
SO_2	0.0627.. 0.0621.. 0.0625..	40.03.. 39.26.. 39.62..	18.27.. 18.09.. 18.14..	18.17..
NH_3	0.0623.. 0.0619.. 0.0623.. 0.0620..	39.42.. 39.02... 39.13.. 39.21..	18.11.. 18.04.. 17.98.. 18.10..	18.06.
HCl	0.0620.. 0.0624.. 0.0624.. 0.0627.. 0.0622..	39.84.. 39.11.. 38.95.. 39.50.. 39.35..	18.40.. 17.94.. 17.86.. 18.03.. 18.10..	18.07..

From a glance at the figures in the tables, it is evident that the method was fairly reliable. The accuracy obtained by Sayce and Briscoe's method could not be expected, but when the figures for any one liquid in any one gas are examined, very good agreement in the majority of cases, is found between them. At the same time, the pressures for all four liquids in air are greater than the theoretical value, 18.58mm., a state of affairs which is difficult to explain. Nevertheless, all the other results are less, and in some instances to a considerable extent, than the values found for the respective liquids in air.

A most surprising result was obtained when the determination of the vapour pressure of methyl alcohol in HCl was attempted, although the preliminary experiments had shown there was great attraction between the molecules. The pressure in the flask was less than the initial pressure, showing that HCl gas had been removed in some fashion. It might have been due to some of the methyl alcohol remaining unvapourised and dissolving some of the HCl gas, but even when as small a quantity of methyl alcohol as 0.0182gm. was added, the final pressure was still lower than the initial pressure. On close examination it was noticed that when the flask was cooled again to 25°C after the vapourisation of the liquid, little droplets of liquid formed on the sides of the flask and flowed down to the bottom. It would seem that the HCl gas was behaving as it does in air, when it dissolves in the moisture of the air

giving little droplets of hydrochloric acid solution. Here droplets of methyl alcohol containing dissolved HCl gas would be formed, thus producing this large lowering of the pressure.

No figures are given for acetone in ammonia because it is known that they interact readily to form definite compounds.

If the figures for methyl alcohol are examined, it is found that the pressures exerted by a millimol of methyl alcohol vapour in a volume of 1000cc. at 25°C are :-

Table III.

Air.	HCl.	CO_2.	SO_2.	NH_3.
18.98mm.	-7.04mm.	18.27mm.	17.58mm.	14.81mm.

When these figures are compared with those in Table I, there is a rough relationship noticeable between the two sets of figures, even when the unreliability of those in Table I is allowed for. By far the lowest value is found with HCl and the highest with CO_2, i.e., the attraction between the methyl alcohol and the HCl is the greatest and between methyl alcohol and CO_2 the least; NH_3 and SO_2 coming in between in that order. The order is the same in both series, but that is about all that can be said. Thus in Table I the figures for SO_2 and NH_3 are practically the same, being quite different from that for CO_2.
In Table III on the other hand, the difference between the

figures for CO_2 and SO_2 is much less than between SO_2 and NH_3.

Once the vapour pressures had been determined, the next step was to compare the solubilities of the gases in the liquids with the decrease in pressure obtained, when the liquids are evaporating into gases other than air. For this purpose it was necessary to secure the solubilities of the gases in the liquids, and a search was made for the data. Some of it was readily secured from Seidell's Solubility Tables, but it was found impossible to obtain all the solubilities desired. In some cases, the solubility of a gas in a liquid was given at other temperatures than 25°C which was useless because of the great difference in the solubility of gases at different temperatures.

The solubilities of HCl, CO_2 and NH_3 in ether were only obtainable at 15°C, but these were taken because they give the relative solubilities at a temperature not too far removed from 25°C. No value could be obtained for SO_2 in ether, nor any useful figures for the gases in chloroform and acetone. Therefore a comparison can only be made with ether and methyl alcohol.

In order to compare the results, the solubilities in the Table below have been expressed as gram molecules of dissolved gas per gram molecule of liquid solvent. This was necessary for one thing, because the solubilities as found were expressed in all kinds of units;

number of cc. of gas soluble in xcc. solvent; number of grams soluble in y gms. solvent or solution, and in some cases use had to be made of partition coefficients. When this is taken into account and also the fact that the determinations were carried out by different workers using different methods, the values for the solubilities can only be taken as approximate.

In the Table, opposite 'Solubility' the number of gm. molecules of the gas soluble in 1 gm. molecule of the solvent is given. Underneath that, opposite 'attraction', the difference in mm. between the vapour pressure exerted by a millimol of liquid in 1000cc. at 25°C in the gas and the vapour pressure in air. Thus the figure for ether in air is 18.82mm. and in HCl 13.92mm., therefore the difference or attraction is 4.9mm.

Table lV

Solubilities of gases in ether and methyl alcohol compared with the attractions between the gases and the vapours of the solvents.

Ether as solvent.

	HCl	SO_2.	CO_2	NH_3.
Solubility.	0.774	-	0.0236	0.045gm. mol./gm.mol.
Attraction.	4.9	1.48	0.49	0.50mm.

Methyl alcohol as solvent.

	HCl	SO_2	CO_2	NH_3
Solubility.	0.717	0.225	0.0064	0.376gm.mol./gm.mol.
Attraction.	26.	1.4	0.71	4.17mm.

From consideration of these figures it will be seen that HCl is the most soluble gas in both ether and methyl alcohol, and that carbon dioxide is the least, and that the attraction between the molecules is greatest with HCl as the gas and least when CO_2 is the gas , if air is not considered. At the same time there is no close agreement between the figures, e.g. the solubility of NH_3 in ether is approximately twice that of CO_2 in ether and yet the lowerings of the vapour pressures produced by the respective gases are almost exactly the same.

In the case of methyl alcohol as solvent the same thing occurs. HCl is the most soluble in the solvent and CO_2 the least, and the attraction is greatest between the HCl and the alcohol and least when CO_2 is the gas. Again, the attraction between SO_2 and the vapour is twice that between CO_2 and the alcohol, but the solubility of SO_2 is more than thirty times greater than that of CO_2 in the alcohol.

To sum up briefly the results of this investigation:- an apparatus was constructed for the determination of vapour pressures which gave reasonably accurate results with less trouble than that encountered in Sayce and Briscoe's method. By means of it, the vapour pressures of certain liquids were determined in the presence of different gases. It was found that the vapour pressures of the liquids examined are all lower in the gases than in

air, in some cases to a remarkable extent, thus showing great attraction between the molecules of the vapour and those of the different gases. On examination there is found to be some slight relationship between the attraction and the solubility of the gases in the respective liquids, in that very soluble gases show great attraction for the vapours of the liquids in which they are soluble, but it cannot be said that the relation is a quantitative one.

BINARY LIQUID SYSTEMS
and the
MIXTURE RULE.

The work embodied in this paper has been published in the Journal of the Chemical Society, in February, 1933.

Much of the investigation which has been carried out on the subject of binary liquid mixtures has been concerned with attempts to discover formulae connecting the properties of the mixture with those of its components. The simplest formula which can express the relationship between the physical properties of the mixture and those of its components is the so called mixture rule,

$$K = K_1 x + K_2(1-x)$$

where K is the value of the property for the mixture, and K_1 and K_2 the values for the pure constituents and x and (1-x) the quantities of these constituents present in the mixture. Agreement between the calculated values and the actual values found by experiment can only be expected if the liquids behave as 'normal' or 'ideal' liquids. According to Findlay, ('Osmotic Pressure' page 30.) a system is ideal when there is no association, dissociation or combination on mixing the constituents. The quantities x and (1-x) can be expressed either as weight, volume or molar fractions and the correct method of representation will depend on the property under investigation.

It is this side of the subject which is to be considered in the following paper, rather than the different mathematical expressions suggested, although the latter must receive some attention also, since the method

of representation is important, no matter what formula is being considered. We will return to these different formulae when we discuss the viscosity of liquid mixtures.

In some papers x has been expressed as a volume fraction, weight fraction and molar fraction without justification for any one of these procedures. For some physical properties there is no doubt as to the correct method of expressing the composition of liquid mixtures; e.g., since density is mass per unit volume of the substance, x should be expressed as a volume fraction, and specific volume as a weight fraction. For specific heat, heat capacity per gram, weight fractions should be employed, but for vapour pressure, where we are dealing with the concentration of the molecules in the gas phase, the composition of the liquid mixture should be expressed in molar fractions; i.e., when an equilibrium between two states is under consideration, the composition of each state should be expressed in the same manner.

The correct method of expressing the composition of a liquid mixture whose refractive index or dielectric constant is being investigated is not so certain. The refractive index of a substance is the ratio of the speed of light in a vacuum to its speed in the medium; hence, since the measurement of speed involves that of distance, it would seem that volume proportions should be used in expressing the composition of a mixture whose refractive index is being considered. Volume

proportions should be employed in the case of dielectric constant, for its measurement involves the comparison of a vacuous condenser with the same condenser when filled with the substance under consideration. The close relation between dielectric constant and refractive index also indicates that for these properties the composition of a solution should be expressed in the same manner.

In a binary mixture the composition of the surface will be the same as the volume composition of the system. It would therefore seem that for surface tension the composition of a mixture should be expressed in volume proportions. On the other hand, since the surface tension of a liquid is a measure of the work required to create unit surface by bringing molecules from the body of the solution into the surface, and it is obvious that this work will depend on the type of molecule moved, it may be argued that molecular proportions would be a more correct method of expressing the composition of the solution in this case. Attempts have been made to express the relationship between the surface tension of a mixture and those of its components, but none of the formulae suggested have proved to be of general application. The ordinary formula with the composition expressed in volume proportions has been tested by different investigators, a factor R being introduced if the liquids expand or contract on mixing.

$$\gamma = (v_1\gamma_1 + v_2\gamma_2)R$$

Whatmough (Zeit. Phys. Chem. 39, 129, 1901)

found that a few mixtures agree quite closely with the admixture rule in this form, the difference between the observed and calculated values for γ being about one-half per cent. The majority of the mixtures examined do not conform to the admixture rule even when this allowance is made. Generally the surface tension is less. For a list of the investigators and their papers, the chapter on surface tension in Smile's book, 'the Relations between Chemical Constitution and some Physical Properties' may be consulted.

The correct method for viscosity is not apparent at first sight. The coefficient of viscosity of a liquid is the tangential force which must be applied to one face of a cube of 1cm. edge in order to give it unit velocity relative to the opposite face; therefore it would seem correct to express mixture composition in volume fractions when dealing with this property. On the other hand, Kendall (Medd.K.Vetenskapsakad.Nobelinst. 2, 25, 1913) states that since 'viscosity is essentially the frictional resistance encountered by the molecules of a solution in moving over one another' (Noyes, Journ. Amer. Chem. Soc. 34, 457, 1912) it seems to be more logical to represent compositions in molar, rather than weight or volume fractions.

Liquid mixtures seldom, if ever, obey the mixture rule for viscosity, no matter how the composition of the system is expressed. This, indeed, is to be

expected in view of the nature of the property. We might as well expect the strength of a chain to be the average of the strengths of the links, as to expect the resistance to applied shearing stress in the case of a liquid mixture to be the average of the resistances of the constituents. It would seem more probable that the viscosity of the mixture should approximate to that of the less viscous constituent.

To illustrate further the diversity of opinion regarding the correct method of expressing the concentration, and at the same time, to give some idea of the different formulae suggested by various investigators we will consider the work done on the viscosity of liquid mixtures in a little more detail. At the same time it is impossible to do more than give a brief résumé of the work, because the amount done has been enormous. According to Hatschek (Viscosity of Liquids, 1928) the number of references to the viscosity of binary liquid mixtures in the supplementary volume of Landolt and Börnstein's tables (1927) amounts to about eleven hundred. Kremann in his 'Die Eigenschaften der Binaren Flussigkeitsgemische'(1916) gives over four hundred references to work done on the physical properties of binary mixtures.

Bingham (Amer.Chem.J. 35, 195, 1906, and Phys. Rev. 1912, 35 407) suggests that fluidities rather than viscosities agree with the simple mixture rule.

$$\phi = x\phi_1 + (1-x)\phi_2 \qquad \text{or} \qquad \frac{1}{\eta} = \frac{x}{\eta_1} + \frac{(1-x)}{\eta_2}$$

where ϕ_1 and ϕ_2 are the reciprocals of the viscosities; x and (1-x) are the concentrations expressed in volume fractions.

On the other hand, Lees (Phil. Mag. 6, 1. 128, 1901) found that volume concentrations were unsatisfactory for fluidities.

Drucker and Kassel (Zeit. phys. Chem. 76, 367, 1911) proposed the same formula using weight composition units, but it proved to be equally inadequate.

In 1887 Arrhenius (Zeit. physik. Chem 1, 285, 1887) put forward a purely empirical formula,

$$\eta = \eta_1^{\,x}\ \eta_2^{\,(1-x)}$$

which may be written

$$\log\eta = x\log\eta_1 + (1-x)\log\eta_2$$

the composition being expressed in volume fractions. This expression was found to hold fairly well for mixtures up to 0.1 of one component, but it was useless for the whole range x=0 to x=1.

Dunstan and Thole (Viscosity ofLiquids, pp. 32-38) however, in the examination of homologous series of liquids, found that their results agreed with the above formula.

Kendall and Monroe (J.Amer.Chem. Soc. 1917, 39, 1787) give a useful summary of the work done on the

viscosities of mixtures and have given much consideration to the question themselves. They tested all the formulae on eighty-four mixtures of presumably non-associated and chemically indifferent liquids. These gave, in general, curves which were slightly 'sagged' or convex to the x or composition axis. The greater the difference in viscosity of the components, the greater is the sag towards the x axis, no matter the way in which the concentrations are expressed. The deviation from the straight line is generally least when this done in molar fractions.

They propose the following formula

$$\eta^{1/3} = x\eta_1^{1/3} + (1-x)\eta_2^{1/3}$$

in which x is the molar fraction.

This equation very exactly represents the viscosity of the benzene-benzyl benzoate mixture, but it fails when toluene is substituted for the benzene.

This brief account of the proposed formulae in the one case of viscosity and the uncertainity of the correct units to employ therein gives some idea of the complexity of the problem of liquid mixtures.

In the investigation of the properties of liquid mixtures the first difficulty to be overcome is the securing of 'ideal' liquids. In the following work certain presumably 'ideal' liquids have been examined and an attempt made from the results obtained, to find the correct method of representation of the concentration

assuming that 'ideal' liquids obey the simple binary mixture rule,

$$K = K_1 x + K_2 (1-x)$$

Requirements of Ideal Liquids.

In an investigation of any particular property of a mixture to test the validity of the mixture rule and the correct method of expressing the composition the liquids must satisify certain requirements:

a) They must be ideal in the sense quoted above (Findlay) having, as nearly as possible, the same chemical nature in order to minimise the chance of any reaction between them.

b) The property under investigation should have greatly different values for the two pure constituents, otherwise the property-composition curve will tend to be represented by a horizontal line no matter how the composition is expressed.

c) Constituents of similar density (for another reason than that stated in b), molecular weight or molecular volume must be avoided, otherwise there will be a close similarity between curves plotted by different methods.

The first two are obvious, but the third one only became apparent when the physical properties of mixtures of Ethylene dichloride and Ethylene dibromide

were determined. (see below).

On first considerations two alcohols or benzene and toluene would appear to be suitable as they satisfy the first requirement (a) excellently, but they fail in certain specific properties to satisfy the second (b). In the case of Methyl and Ethyl Alcohols for instance, although viscosity proves to be satisfactory since the viscosities of the alcohols are 0.00548 and 0.01099 poises at 25° respectively, (calculated from Bingham's figures, Zeit. phys. Chem. 83, 1913, p.641.) the densities are 0.7929 and 0.7907gm./c.c. at 20°C, and the values for the surface tensions 23.645 and 23.090 dynes/cm. respectively. (J, Amer. Chem. Soc. 1917, 39, 2275). Therefore the two alcohols are unsuitable for an investigation of this kind, because no matter how the concentrations are expressed for certain properties, even if the difference between the values of the several concentrations is considerable, the property-composition curves will tend to be represented by a line parallel to the composition axis.

Mixtures of Acetic and Propionic Acids are unsuitable for the same reasons, as the following figures show,

	Density at 25C	Refractive Index	Viscosity	Surface Tension
Acetic Acid	1.043g/cc.	1.36973	0.01115	26.4
Propionic Acid	0.986 ..	1.38458	0.01026	25.51

Requirement (c) is important but is not always easy to satisfy.

When mixtures of Ethylene dichloride and Ethylene dibromide were examined and values obtained for some of their physical properties, it was found that the volume curves were almost identical with the molecular ones. On consideration, the reason for this was evident. Here are two liquids differing greatly in molecular weight and density but they have very similar molecular volumes.

$$\text{Molecular Volume} = \frac{\text{Molecular Weight}}{\text{Density}}$$

$$\frac{C_2H_4Cl_2}{D_{25}} = \frac{98.92}{1.238} = 79.9$$

$$\frac{C_2H_4Br_2}{D_{45}} = \frac{187.8}{2.169} = 86.6$$

On the other hand, the hydrocarbons which have been examined do not differ so greatly in density and therefore the property-composition curves expressed by volume are similar to those expressed by weight. (see Graphs)

Methods of Recording Results.

Deviations from the mixture rule may be positive or negative or may change sign with different composition of solution. Kremann in his 'Flussigkeits-gemische' (p. 5) describes the various types of 'Eigenschaftskurven' found by a study of liquid mixtures.

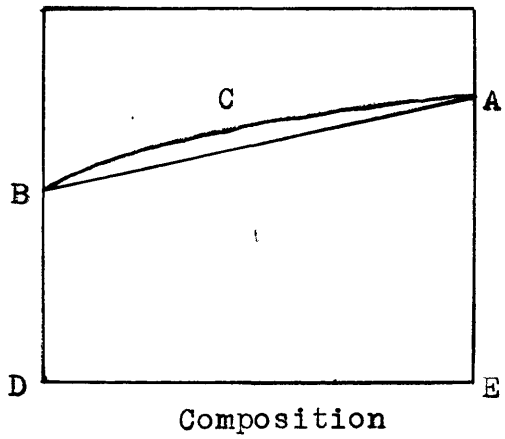
a) The first method of recording results is by simply plotting them and drawing the curves. This is the most satisfactory way of showing the relationship between the property and the composition of the mixture, as any deviation can be seen at a glance.

b) When it is not convenient to draw a graph the results may be tabulated and any deviation shown by considering an arbitrarily chosen mixture, say 50%.

c) In this method an average value for the deviation is obtained by integrating the property composition curve. This is more satisfactory than (b).

Thus the 'average deviation' is given by the area ABC divided by the length DE. (see figure on next page). The 'average relative deviation' is obtained by dividing the area ABC by the area ABDE.

It should be noted that the 'average relative deviation' is a simple number and may be used to compare different properties of a given mixture with one another.



Results.

The results obtained with four pairs of substances are given in the following tables I, II, III, and IV (pp. 52-56.)

The first section of each table gives the percentage concentration of the mixture in weight, volume and molecular proportions; the volume and molecular percentages being calculated from the weights of each constituent of the mixture. Under 'Found' for each property are given the values obtained experimentally, while under 'Calc.' the theoretical values calculated from the mixture rule are given for mass, volume and molecular composition for each mixture. D is the density in gm. per c.c.; n is the refractive index; γ is the surface tension; η is the viscosity; and $1/\eta$ the fluidity, all at 25°C.

From the experimental data given in these tables, three property-composition curves were drawn for each liquid pair, using (a) weight, (b) volume and (c)

molecular proportions. The weight curve is depicted in all cases by a black line; the volume by a green and the molecular curve by a red line. These graphs are given at the end of this paper.

From such curves the average deviations' and the 'average relative deviations' were obtained in the manner described above. These values are tabulated in tables V and VI.

The areas required in the calculations were determined by means of a planimeter. In many cases the graphs from which the areas were taken are not those shown here, but were much larger ones, which gave larger areas, and so reduced the possibility of large errors in their measurement with the planimeter. The paper on which the graphs were drawn afforded 16 inches for the property axis and 10 inches for the composition axis. Several determinations of each area were made and the average value used in the calculation.

In the tables no claim is made that the values for the physical properties of the liquids are absolute, because a slight error, so long as it is constant, does not interfere with the consideration of the curves or 'average deviations' in an investigation of this description. It is very easy to determine density or refractive index with a high degree of accuracy, but it is not so with surface tension and viscosity on account of experimental difficulties. Nevertheless the values for

the pure liquids were found to agree very well with those of other investigators, where figures could be obtained at the corresponding temperatures. Thus:-

Viscosity of Benzene at 25°C.

0.00596poises	Lewis 1925	0.006075poises	Found
0.00608 ..	Kurnakow 1924		
0.00615 ..	Dunstan and Shrubb 1908		
0.00602 ..	Bingham and Sarven 1920		

Surface Tension of Benzene at 25°C.

against air 28.23 dynes/cm. against air 27.43 Found.

against N_2 27.2 .. .. (Sugden)

Preparation of the Mixtures.

The mixtures were all prepared by pipetting out definite volumes of each liquid which were accurately weighed. It was easy therefore, to obtain any desired mixture by calculating roughly the volume required to give that mixture. Knowing the weight of each constituent, the exact volume percentage could be calculated from figures obtained by dividing the weight of each constituent by its density. In the same way, by dividing the weight of each constituent by its respective molecular weight, figures were obtained from which the molecular percentage could be calculated.

Table I.

Tetralin-Benzene mixtures at 25°.

$C_{10}H_{12}$, %.			D, g./c.c.		n.		γ, dynes/cm.	
Wt.	Vol.	Mol.	Found.	Calc.	Found.	Calc.	Found.	Calc.
0	0	0	08736		1·49781		27·43	
				W. 08934		W. 1·5066		W. 29·06
21·52	19·86	13·94	08921	V. 08921	1·50635	V. 1·5064	28·56	V. 28·94
				M. 08864		M. 1·5036		M. 28·50
				W. 09124		W. 1·5156		W. 30·61
42·23	39·79	30·16	09101	V. 09106	1·51500	V. 1·5150	29·78	V. 30·43
				M. 09014		M. 1·5104		M. 29·74
				W. 09310		W. 1·5242		W. 32·14
62·20	59·80	49·28	09290	V. 09295	1·52362	V. 1·5236	31·16	V. 31·95
				M. 09189		M. 1·5186		M. 31·16
				W. 09486		W. 1·5324		W. 33·60
81·48	79·93	72·90	09475	V. 09480	1·53217	V. 1·5322	32·90	V. 33·48
				M. 09408		M. 1·5287		M. 32·96
100	100	100	09661		1·54062		35·02	

$C_{10}H_{12}$, %.			$\eta \times 10^5$, poises.		$1/\eta$.	
Wt.	Vol.	Mol.	Found	Calc.	Found.	Calc.
0	0	0	6075		1644	
				W. 900		W. 1400
21·52	19·86	13·94	7190	V. 876	1391	V. 1420
				M. 796		M. 1486
				W. 1189		W. 1163
42·23	39·79	30·16	8758	V. 1156	1142	V. 1192
				M. 1022		M. 1302
				W. 1466		W. 934
62·20	59·80	49·28	1098	V. 1434	911	V. 962
				M. 1287		M. 1083
				W. 1728		W. 718
81·48	79·93	72·90	1445	V. 1708	692	V. 735
				M. 1612		M. 812
100	100	100	1985		504	

Table II.

Decalin-Cyclohexane mixtures at 25°.

$C_{10}H_{18}$, %.			D, g./c.c.		n.		γ, dynes/cm.	
Wt.	Vol.	Mol.	Found.	Calc.	Found.	Calc.	Found.	Calc.
0	0	0	0·7738		1·42342		23·94	
				W. 0·7970		W. 1·4348		W. 25·30
22·10	19·95	14·72	0·7956	V. 0·7948	1·43432	V. 1·4339	24·81	V. 25·17
				M. 0·7894		M. 1·4310		M. 24·85
				W. 0·8192		W. 1·4458		W. 26·60
43·04	39·92	31·52	0·8149	V. 0·8158	1·44464	V. 1·4445	25·92	V. 26·41
				M. 0·8070		M. 1·4399		M. 25·90
				W. 0·8398		W. 1·4558		W. 27·83
62·67	59·62	50·52	0·8375	V. 0·8368	1·45465	V. 1·4544	27·01	V. 27·65
				M. 0·8270		M. 1·4497		M. 27·06
				W. 0·8605		W. 1·4657		W. 29·02
81·88	79·89	73·33	0·8561	V. 0·8584	1·46471	V. 1·4647	28·39	V. 28·90
				M. 0·8518		M. 1·4614		M. 28·49
100	100	100	0·8800		1·47509		30·16	

$C_{10}H_{18}$, %.			$\eta \times 10^6$, poises.		$1/\eta$.	
Wt.	Vol.	Mol.	Found.	Calc.	Found.	Calc.
0	0	0	928·7		1076	
				W. 1200		W. 9400
22·10	19·95	14·72	1061	V. 1173	9426	V. 9520
				M. 1108		M. 9850
				W. 1462		W. 8120
43·04	39·92	31·52	1260	V. 1425	7936	V. 8280
				M. 1318		M. 8820
				W. 1706		W. 6930
62·67	59·62	50·52	1480	V. 1668	6746	V. 7120
				M. 1556		M. 7660
				W. 1946		W. 5730
81·88	79·89	73·33	1770	V. 1922	5649	V. 5860
				M. 1849		M. 6250
100	100	100	2171		4606	

Table III.

Tetralin-Cyclohexane mixtures at 25°.

$C_{10}H_{12}$, %.			D, g./c.c.		n.		γ, dynes/cm.	
Wt.	Vol.	Mol.	Found.	Calc.	Found.	Calc.	Found.	Calc.
0	0	0	07738		1·42342		2394	
				W.·08195		W.1·4512		W.·2658
23·67	19·88	16·44	·08114	V.·08123	1·44685	V.1·4468	25·45	V.·2618
				M.·08058		M.1·4431		M.·2578
				W.·08614		W.1·4769		W.·2900
45·24	39·82	34·46	·08496	V.·08504	1·47016	V.1·4703	26·94	V.·2842
				M.·08399		M.1·4040		M.·2778
				W.·08990		W.1·5000		W.·3123
65·22	60·01	54·41	·08888	V.·08890	1·49560	V.1·4938	28·86	V.·3063
				M.·08786		M.1·4875		M.·3000
				W.·09343		W.1·5210		W.·3322
83·24	79·91	75·97	·09272	V.·09272	1·51727	V.1·5173	31·54	V.·3287
				M.·09200		M.1·5127		M.·3242
100	100	100	·09661		1·54062		35·02	

$C_{10}H_{12}$, %.			$\eta \times 10^5$, poises.		$1/\eta$.	
Wt.	Vol.	Mol.	Found.	Calc.	Found.	Calc.
0	0	0	9287		1076	
				W.1178		W.·938
23·67	19·88	16·44	9811	V.1136	1019	V.·962
				M.1100		M.·979
				W.1406		W.·813
45·24	39·82	34·46	1127	V.1350	888	V.·844
				M.1292		M.·874
				W.1617		W.·700
65·22	60·01	54·41	1324	V.1563	755	V.·728
				M.1505		M.·760
				W.1807		W.·596
83·24	79·91	75·97	1619	V.1773	618	V.·618
				M.1732		M.·638
100	100	100	1985		504	

Table IV.

Ethylene dibromide-Ethylene dichloride mixtures at 25°.

$C_2H_4Cl_2$, %.			D, g./c.c.		n.		γ, dynes/cm.	
Wt.	Vol.	Mol.	Found.	Calc.	Found.	Calc.	Found.	Calc.
0	0	0	2·169		1·53604		37·13	
				W. 2·075		W. 1·5260		W. 36·47
10·05	16·36	17·56	2·016	V. 2·016	1·51988	V. 1·5206	35·84	V. 36·10
				M. 2·009		M. 1·5192		M. 36·02
				W. 1·945		W. 1·5128		W. 35·60
24·04	36·86	38·75	1·826	V. 1·826	1·50012	V. 1·5008	34·48	V. 34·80
				M. 1·809		M. 1·4988		M. 34·67
				W. 1·844		W. 1·5024		W. 34·92
35·10	48·60	50·59	1·715	V. 1·715	1·48881	V. 1·4895	33·44	V. 34·04
				M. 1·700		M. 1·4876		M. 33·92
				W. 1·705		W. 1·4882		W. 33·96
49·97	63·65	65·50	1·577	V. 1·577	1·47570	V. 1·4753	32·77	V. 33·12
				M. 1·560		M. 1·4735		M. 33·00
				W. 1·565		W. 1·4740		W. 33·03
65·04	76·59	77·91	1·456	V. 1·456	1·46281	V. 1·4630	31·96	V. 32·30
				M. 1·445		M. 1·4620		M. 32·22
				W. 1·470		W. 1·4646		W. 32·40
74·92	83·96	85·01	1·389	V. 1·389	1·45622	V. 1·4562	31·60	V. 31·84
				M. 1·377		M. 1·4550		M. 31·76
100	100	100	1·238		1·44118		30·80	

Table IV (cont.)

Ethylene dibromide-Ethylene dichloride mixtures at 25°.

$C_2H_4Cl_2$, %.			$\eta \times 10^5$, poises.		$1/\eta$.	
Wt.	Vol.	Mol.	Found.	Calc.	Found.	Calc.
0	0	0	1613		6200	
				W.1530		W. 686
1005	1636	1750	1421	V.1477	7037	V. 728
				M.1467		M. 735
				W.1413		W. 780
2404	3686	3875	1216	V.1310	8224	V. 863
				M.1295		M. 877
				W.1323		W. 852
3510	4860	5059	1117	V.1210	8956	V. 940
				M.1195		M. 954
				W.1202		W. 950
4997	6305	6550	1006	V.1086	9942	V.1038
				M.1070		M.1052
				W.1074		W.1048
6504	7659	7791	9179	V. 978	10890	V.1125
				M. 967		M.1134
				W. 990		W.1115
7492	8396	8501	8648	V. 916	11560	V.1173
				M. 906		M.1180
100	100	100	7812		12800	

Table V.

Average Deviations.

		$C_{10}H_{18}$ + C_6H_{12}.	$C_{10}H_{12}$ + C_6H_{12}.	$C_{10}H_{12}$ + C_6H_6.	$C_2H_4Cl_2$ + $C_2H_4Br_2$.
$D_4^{25°}$	Wt.	-0.002	-0.0077	-0.0015	-0.0863
	Vol.	-	-	-0.0006	-
	Mol.	+0.0062	+0.007	+0.0063	+0.0097
n.	Wt.	-0.0008	-0.00413	-0.0005	-0.00898
	Vol.	-	-	-	-
	Mol.	+0.0034	+0.0045	+0.0035	+0.00111
η	Wt.	-0.0015	-0.00202	-0.00236	-0.00137
	Vol.	-0.00123	-0.00164	-0.00213	-0.00066
	Mol.	-0.0005	-0.00123	-0.00124	-0.00051
$1/\eta$	Wt.	-1.0	+5.16	-1.5	-3.39
	Vol.	-2.3	+2.96	-3.7	-2.88
	Mol.	-5.9	+1.16 -0.45	-11.5	-3.76
γ	Wt.	-0.565	-1.497	-0.613	-0.879
	Vol.	-0.428	-1.105	-0.483	-0.334
	Mol.	-	-0.693	-	-0.246

Table VI.

Average Relative Deviations x 1000.

		$C_{10}H_{18}$ + C_6H_{12}.	$C_{10}H_{12}$ + C_6H_{12}.	$C_{10}H_{12}$ + C_6H_6.	$C_2H_4Br_2$ + $C_2H_4Cl_2$.
$D_4^{25°}$	Wt.	- 240	- 08	- 16	- 5060
	Vol.	-	-	- 06	-
	Mol.	+ 750	+ 80	+ 69	+ 570
n.	Wt.	- 055	- 28	- 03	- 603
	Vol.	-	-	-	-
	Mol.	+ 230	+ 30	+ 23	+ 075
η	Wt.	-9770	-1385	-1820	-11500
	Vol.	-7800	-1126	-1640	- 5500
	Mol.	-3200	- 938	- 960	- 4280
$1/\eta$.	Wt.	-1300	+ 655	- 140	+ 3570
	Vol.	-2970	+ 376	- 345	- 3060
	Mol.	-7600	+ 147 - 57	-1073	- 3960
γ	Wt.	-2090	- 51	- 196	- 2590
	Vol.	-1580	- 37	- 158	- 980
	Mol.	-	- 23	-	- 720

Experimental.

The Density, Refractive Index, Surface Tension and Viscosity of each series of mixtures were determined at 25°C.

In all the experiments the liquids were brought to 25°C by immersing the apparatus, pyknometer, viscometer or capillary tube as the case might be, in a glass sided thermostat filled with water. This was kept well stirred by a mechanical stirrer driven by an electric motor, while the temperature was controlled by means of a thermoregulator of the Patterson type.

In the estimation of the density a silica pyknometer of 10c.c., capacity was used.

The Refractive Index was taken with a Hilger refractometer of the Pulfrich type. The prisms and liquid were kept at 25°C by a current of water which was heated by passing it through a large coil immersed in a thermostat kept at about 26°C. By means of a device which gave a constant head of water and a consequent even rate of flow, the temperature of the water in the heating jackets of the instrument, as recorded on the standardised thermometer inserted in the heating jacket, could be kept accurately at 25°C. A sodium flame was used as the source of light.

Surface Tension was measured by the capillary rise method. The apparatus was in the form

of a U tube; the capillary forming one limb and the wide tube containing the liquid, the other. This form was decide upon after consideration of an investigation carried out by Richards and Coombs (J. Amer. Chem. Soc. 1915, 37, 1656) on surface tension. They advocate that the minimum diameter of the large tube should not be less than 38mm., otherwise the surface of the liquid is not level. The construction of the apparatus in the form of a U allows a smaller tube to be used to obtain the level surface required with which the capillary rise is compared. By placing this tube in the thermostat so that the capillary was in front of the larger tube, it was quite easy to obtain a sharp meniscus in the field of the telescope without having to alter the focussing of the telescope of the cathetometer, when it was raised to the level of the liquid in the capillary tube. It is sometimes rather difficult to see clearly the bottom of the meniscus in the field of the telescope, but with this arrangement no difficulty was experienced.

The height h to which the liquid rose in the capillary tube was measured by means of a cathetometer and the surface tension calculated from the expression,

$$\gamma = \tfrac{1}{2}h.r.d.g.$$

where r is the radius of the tube; d the density of the liquid and g is the value of gravity (981 dynes). This gives the surface tension in dynes/cm.

The radius of the capillary tube,,which was the smallest obtainable, was 0.2244mm. Several pieces of tubing were tested in the usual manner by measuring a thread of mercury along the length of the tube, before one was found which was suitable. A piece, having been obtained. which showed practically no variation in diameter over its length of 9 or 10 inches, a mark was made on the tube towards one end and the radius very accurately determined in the region of this mark. The radius r is calculated from the expression,

$$r=\sqrt{\frac{w}{\pi l d}}$$

where w is the weight of the mercury thread; l the length of the thread and d the density of the mercury.

Special precautions were taken to keep the temperature constant while the thread of mercury was being measured, by immersing the capillary tube in a flat basin of water.

In the actual experiment enough liquid was poured into the larger tube to cause the level in the capillary to rise to within a few mm. of this mark on the tube every time.

For Viscosity an ordinary Ostwald viscometer of 20c.c., capacity was constructed. 20cc. were necessary to give suitable differences between the times of flow of different mixtures of the same constituents. In this it

was quite successful and efficient, e.g. pure Decalin took 19 minutes 8 seconds and pure Cyclohexane 8 minutes 53 seconds to pass through the tube. The viscometer had to be thoroughly cleaned between each determination, otherwise the results were not constant. However, by allowing it to stand overnight filled with Chromic Acid cleaning mixture and washing with distilled water and alcohol, and then drying by means of a current of air drawn through the tube with the aid of a filter pump, remarkably close readings were obtained. For instance, the difference in time of three determinations of the rate of flow of Decalin through the tube was only 4/5sec. in 1147 seconds.

The absolute values for the viscosities of the pure liquids and mixtures were obtained by comparing the rate of flow of the liquid through the viscometer with the rate of flow of water through the same instrument at the same temperature,

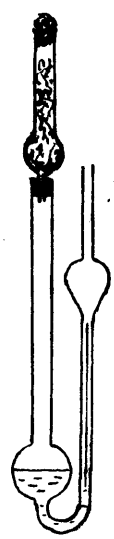
$$\eta_2 = \frac{\eta_1 s_2 t_2}{s_1 t_1}$$

where η_1=coefficient of viscosity of water at 25°.
s_1=density of water at 25°.
t_1=time required for H_2O to flow through the tube.
s_2=density of liquid or mixture.
t_2=time required for liquid to flow through the tube.

The surface tension apparatus received the same careful treatment; only one liquid or mixture being

introduced into it every twenty four hours. Although this procedure appears to be rather slow, still the greater accuracy of the readings obtained made it well worth while, by eliminating 'repeats', both in surface tension and viscosity. (c.f. results of other investigators with those found, above.)

As viscometer and surface tension apparatus had to be allowed to stand in the thermostat for 15-20 minutes before the readings were taken, some precautions had to be taken to prevent the moisture of the air from affecting the carefully dried liquids. The device shown in the sketches below, was adopted; a rubber stopper through which passed a tube containing Calcium Chloride, being inserted in the mouth of the wide limbs of each apparatus. These remained in position while the readings were being taken. The other limbs were closed by small plugs until immediately before the taking of the readings.



The liquids used were all obtained from B.D.H. and were of A.R. quality where possible.

The Cyclohexane was left to stand over $CaCl_2$ for a time and then distilled, using a reflux condenser. The portion used came over within 0.1°C.

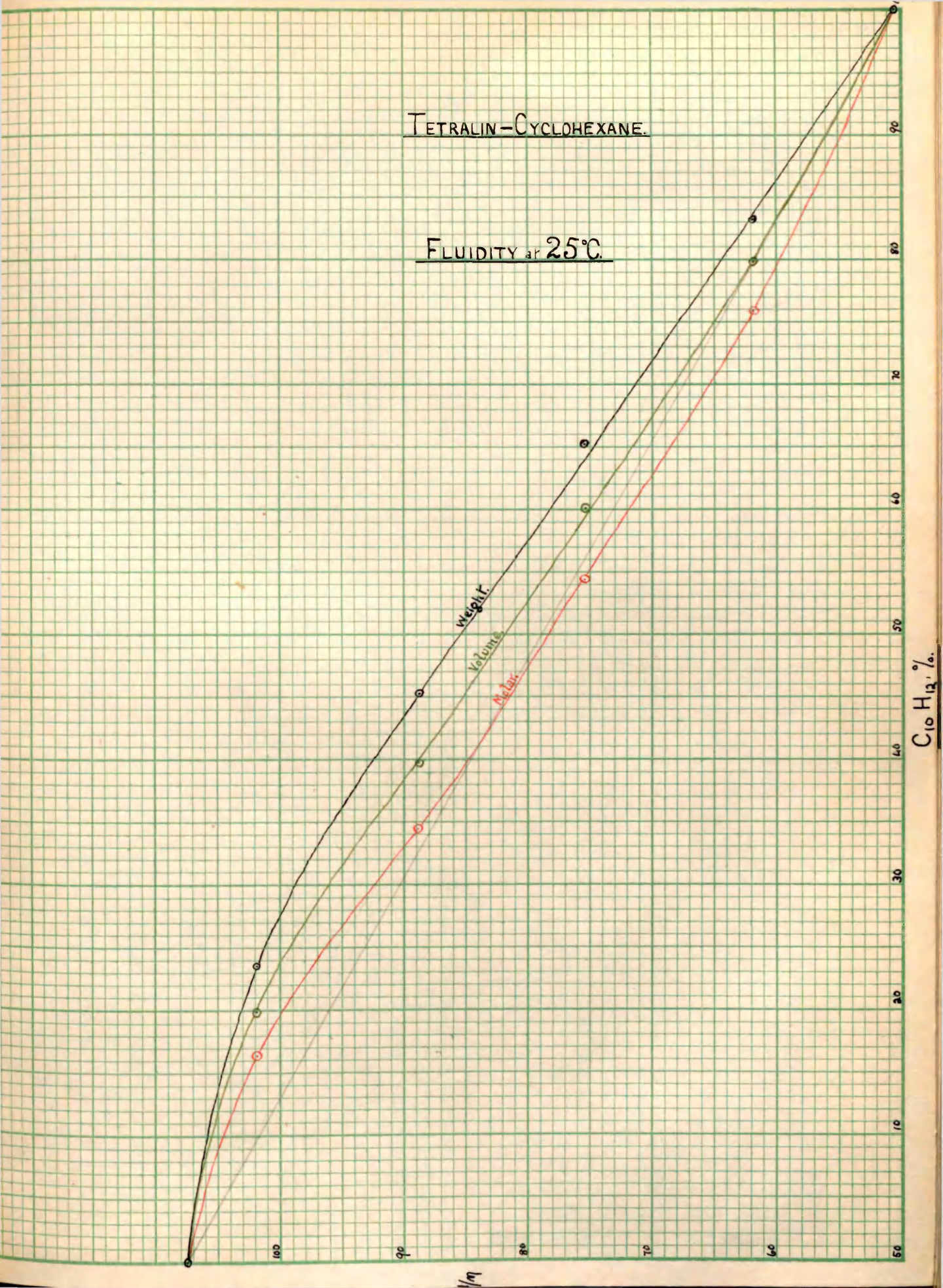
The Benzene had been purified previously and had been standing over mercury for sometime. It was redistilled using a reflux condenser.

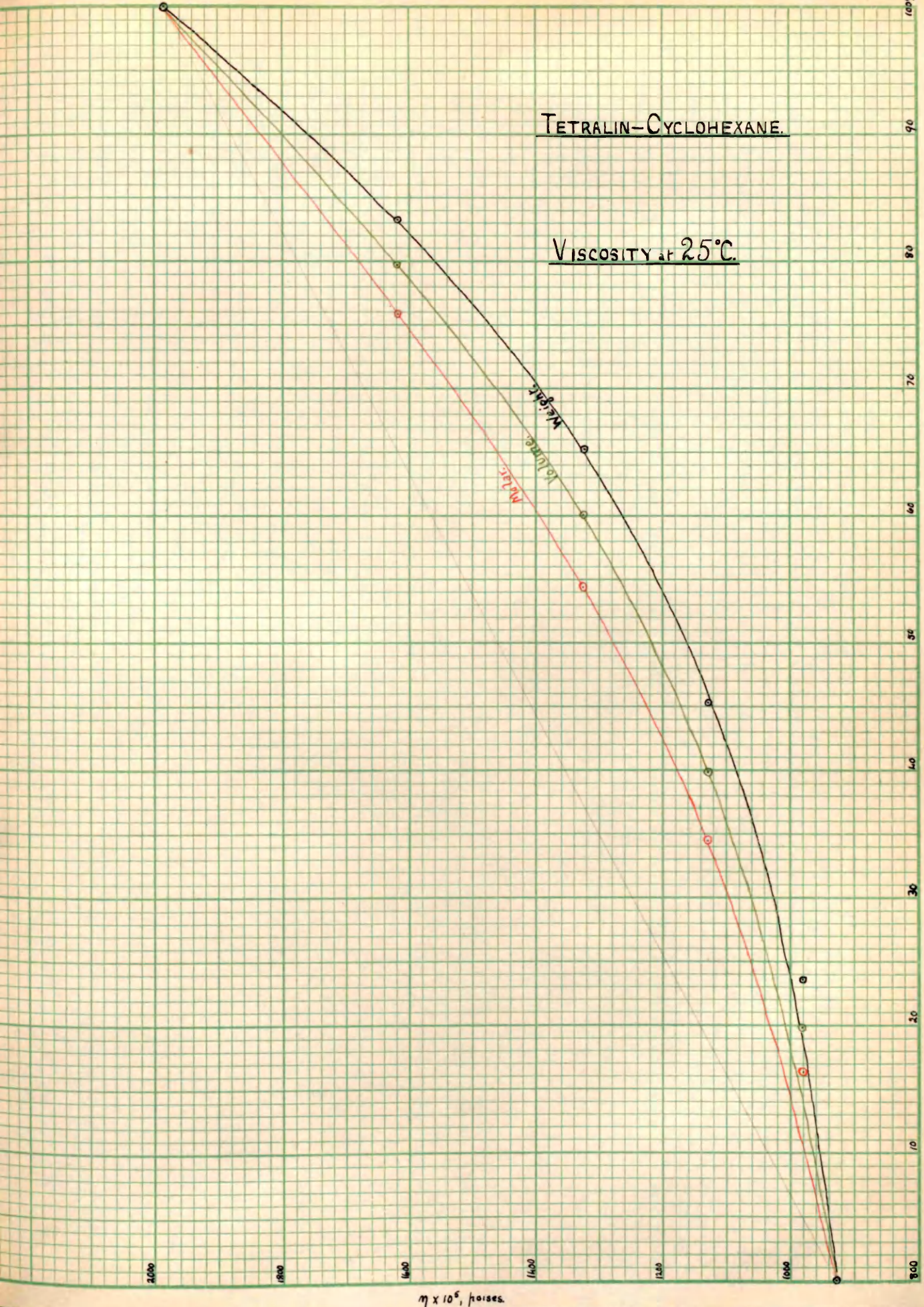
The Ethylene Dichloride and Dibromide were each washed three times with dilute caustic soda solution and several times with water. After drying over $CaCl_2$ for two days, they were distilled. Practically all the Ethylene Dichloride distilled over steadily at 82°C, B. P. 746.7mm. and the Dibromide at 128.3-128.8°C.

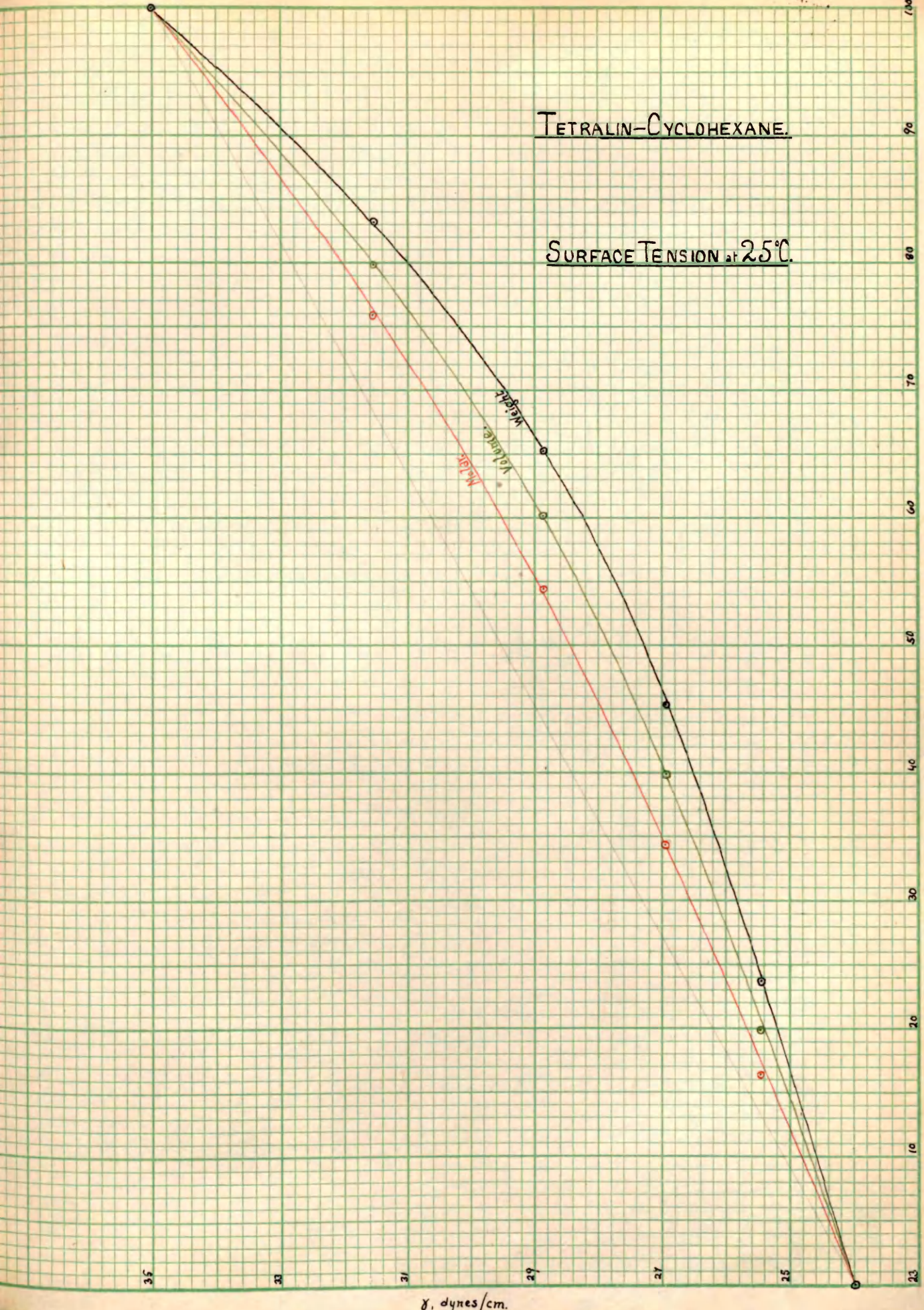
According to Herz and Schuftan (Zeit. phys. Chem. 101, 1922, 269) it is so difficult to remove the last traces of water from Tetralin and Decalin that they must be distilled over sodium at a low pressure to obtain them dry. A trace of water in Tetralin causes an opalescent turbidity when the Tetralin is cooled to 0°C. Both the Tetralin and Decalin were allowed to stand over metallic sodium for a couple of days and then were distilled over fresh sodium. The Tetralin came over at 86-88°C and the Decalin at 72-75°C under a pressure of about 15mm.

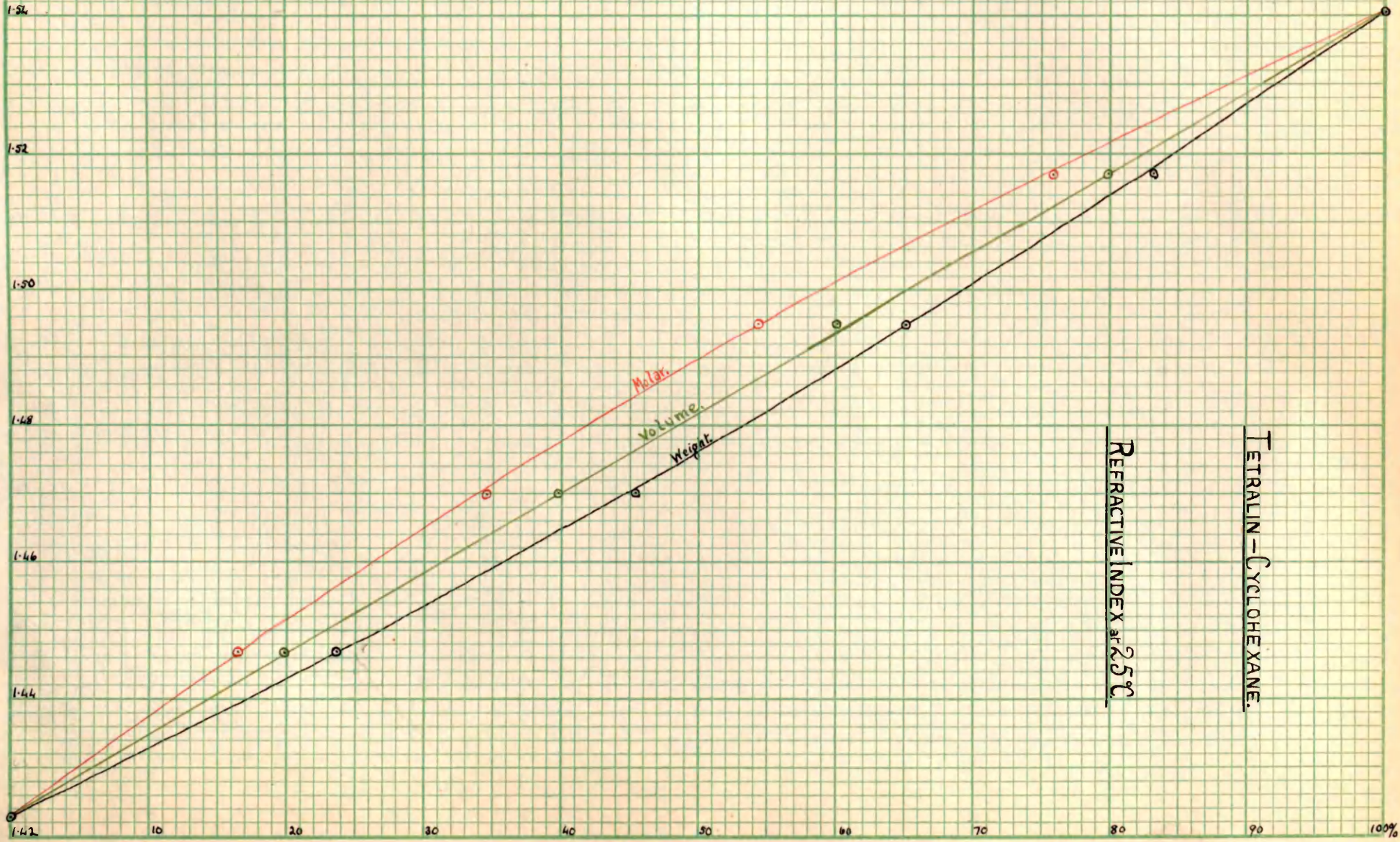
Conclusions.

From a study of the graphs or tables it will be seen that some of the properties of the mixtures agree very well with the mixture rule. Thus in the case of the density (D) the rule is obeyed exactly in three cases when that property is plotted against composition by volume; in the fourth case (tetralin-benzene) the deviation is less when plotted by volume than when either of the other methods is used. For refractive index (n), all four mixtures show agreement with the mixture rule when the property is plotted against volume composition. With surface tension (γ), two mixtures obey the mixture rule when molecular proportions are used, and with the other two systems the deviations are least for this method of plotting. For viscosity (η) and fluidity ($1/\eta$) no method of plotting is satisfactory, but the average relative deviations are greater in the case of viscosity than for its reciprocal, and hence it may be argued that fluidity is the more nearly additive property. The conclusion may therefore be drawn that, for binary liquid mixtures, refractive index and density should be plotted against composition by volume and surface tension against composition expressed in molecular proportions, whilst for viscosity no method seems to be satisfactory.


TETRALIN–CYCLOHEXANE.
FLUIDITY at 25°C.
Weight.
Volume.
Molar.
$C_{10}H_{12}$ %.
100
90
80
70
60
50
40
30
20
10

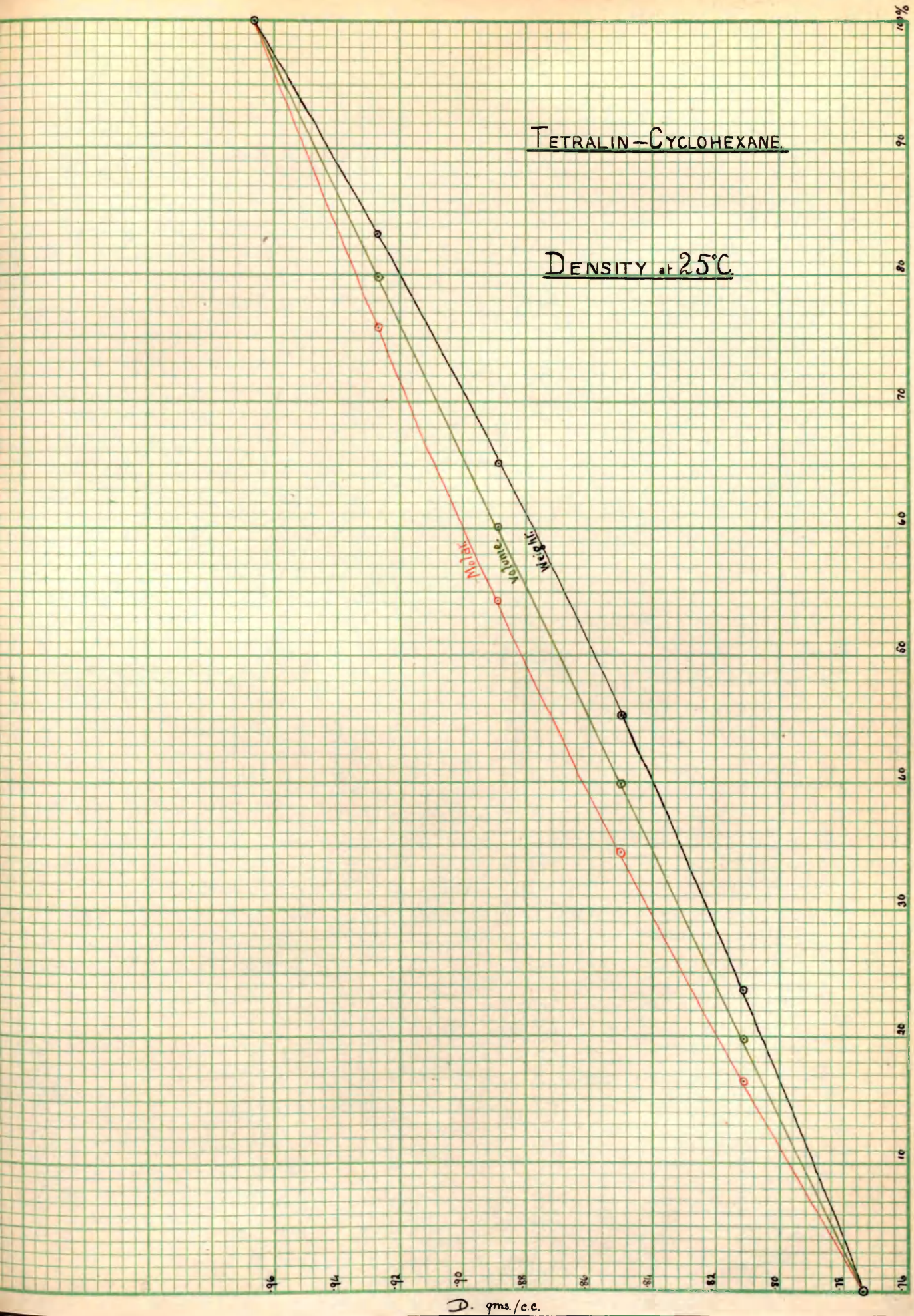

TETRALIN–CYCLOHEXANE.
VISCOSITY at 25°C.
Weight
Volume
Mole
2000
1800
1600
1400
1200
1000
800
100
90
80
70
60
50
40
30
20
10
$C_{10}H_{12}$ %.
$\eta \times 10^6$, poises.

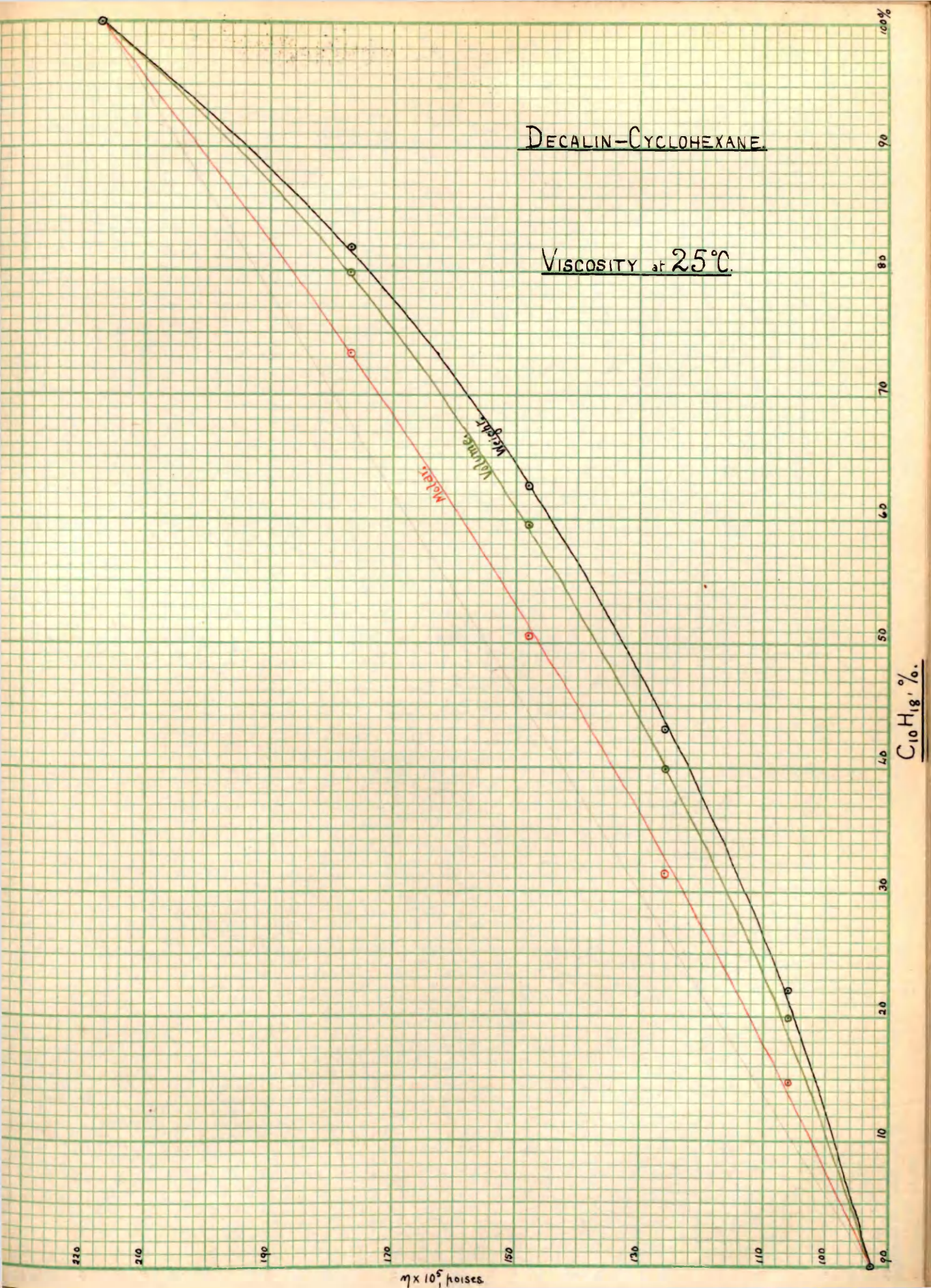

TETRALIN–CYCLOHEXANE.
SURFACE TENSION at 25°C.
Weight.
Volume.
Mol.
100
90
80
70
60
50
40
30
20
10
0
35
33
31
29
27
25
23
γ, dynes/cm.
C10H12 %.



Refractive Index at 25°C.

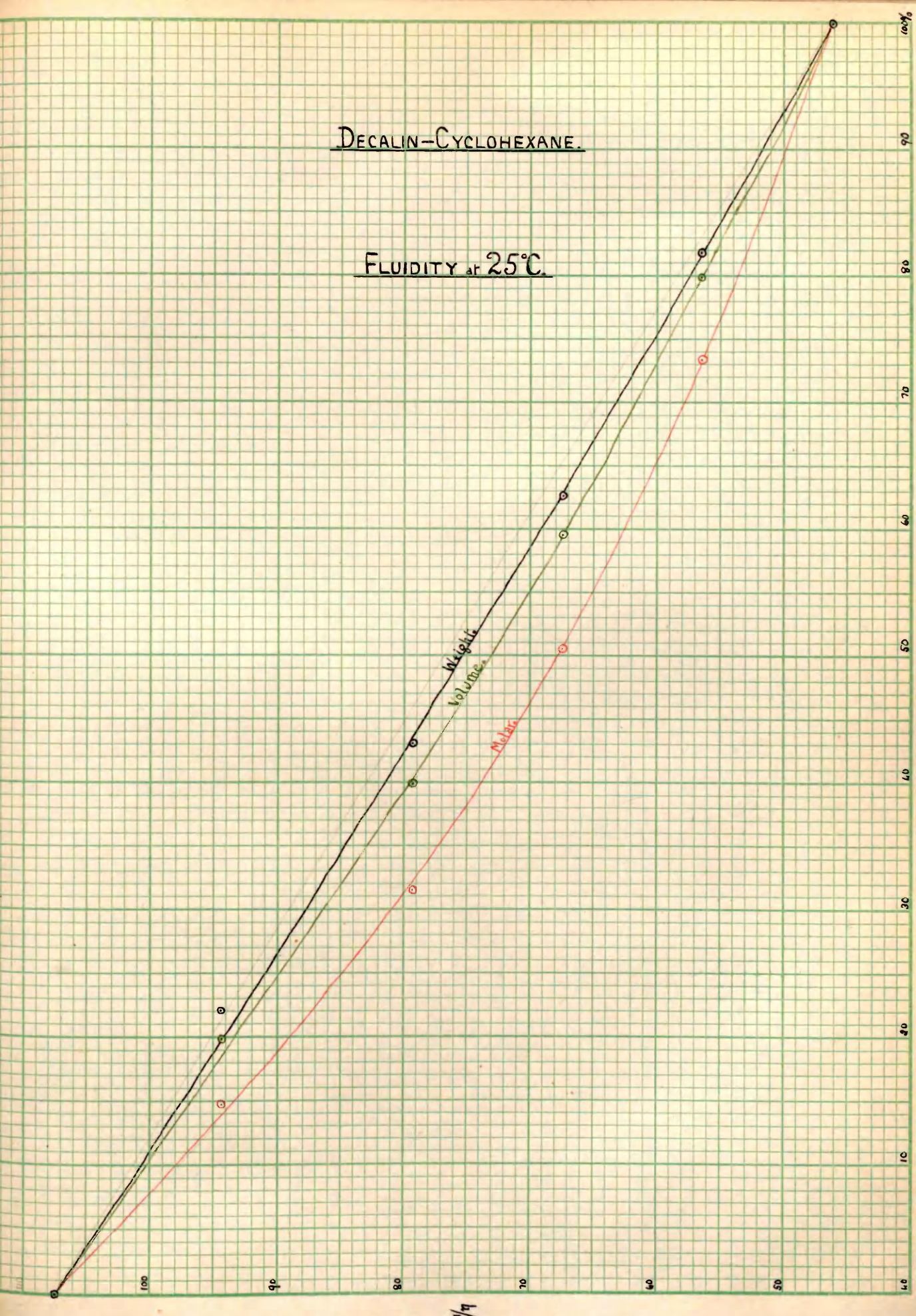
Tetralin—Cyclohexane.

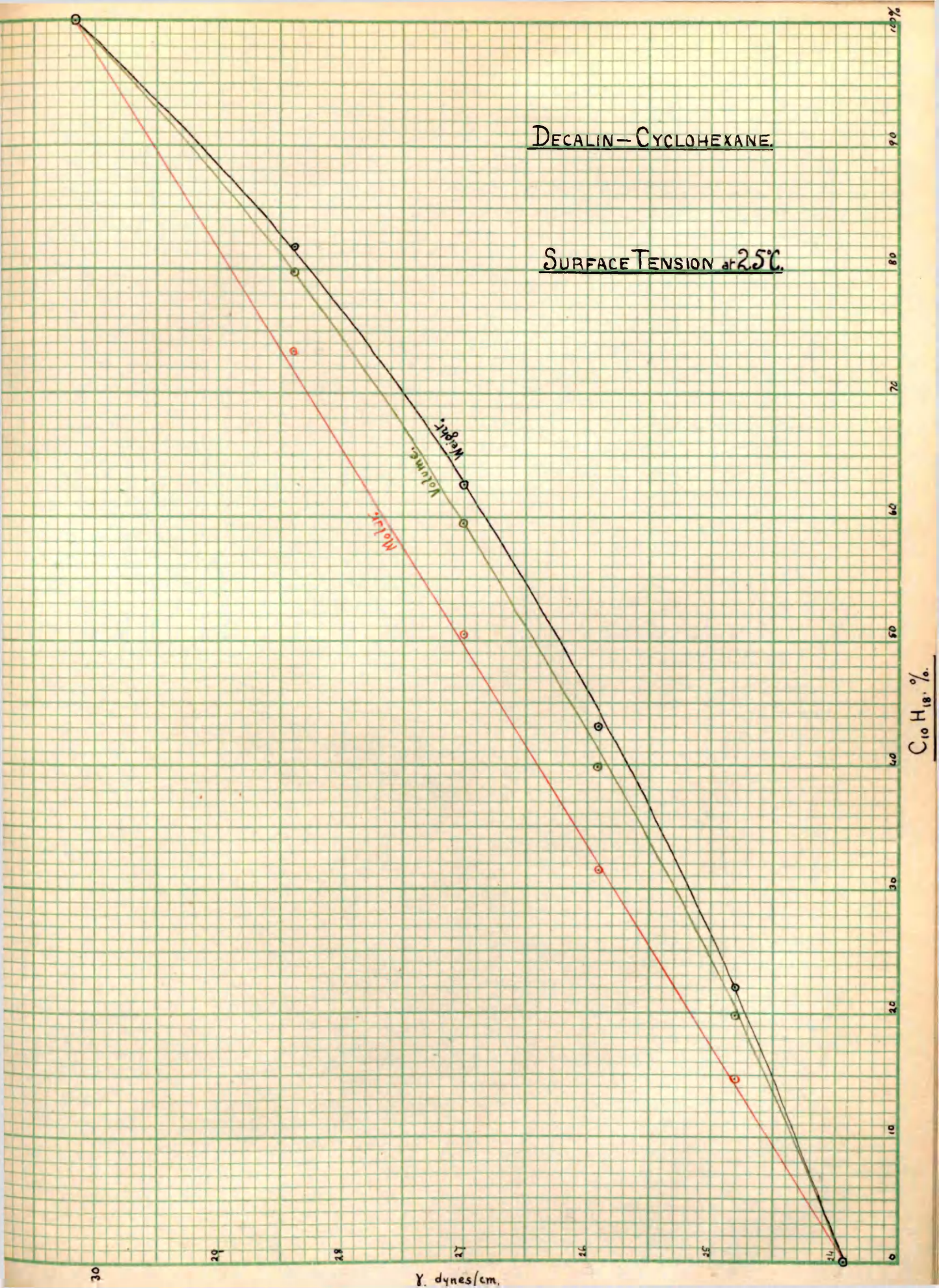

TETRALIN—CYCLOHEXANE.
DENSITY at 25°C.
Weight.
Volume.
Molecular.
100%
90
80
70
60
50
40
30
20
10
0
.96
.94
.92
.90
.88
.86
.84
.82
.80
.78
.76
D. gms./c.c.
C10 H12. %.

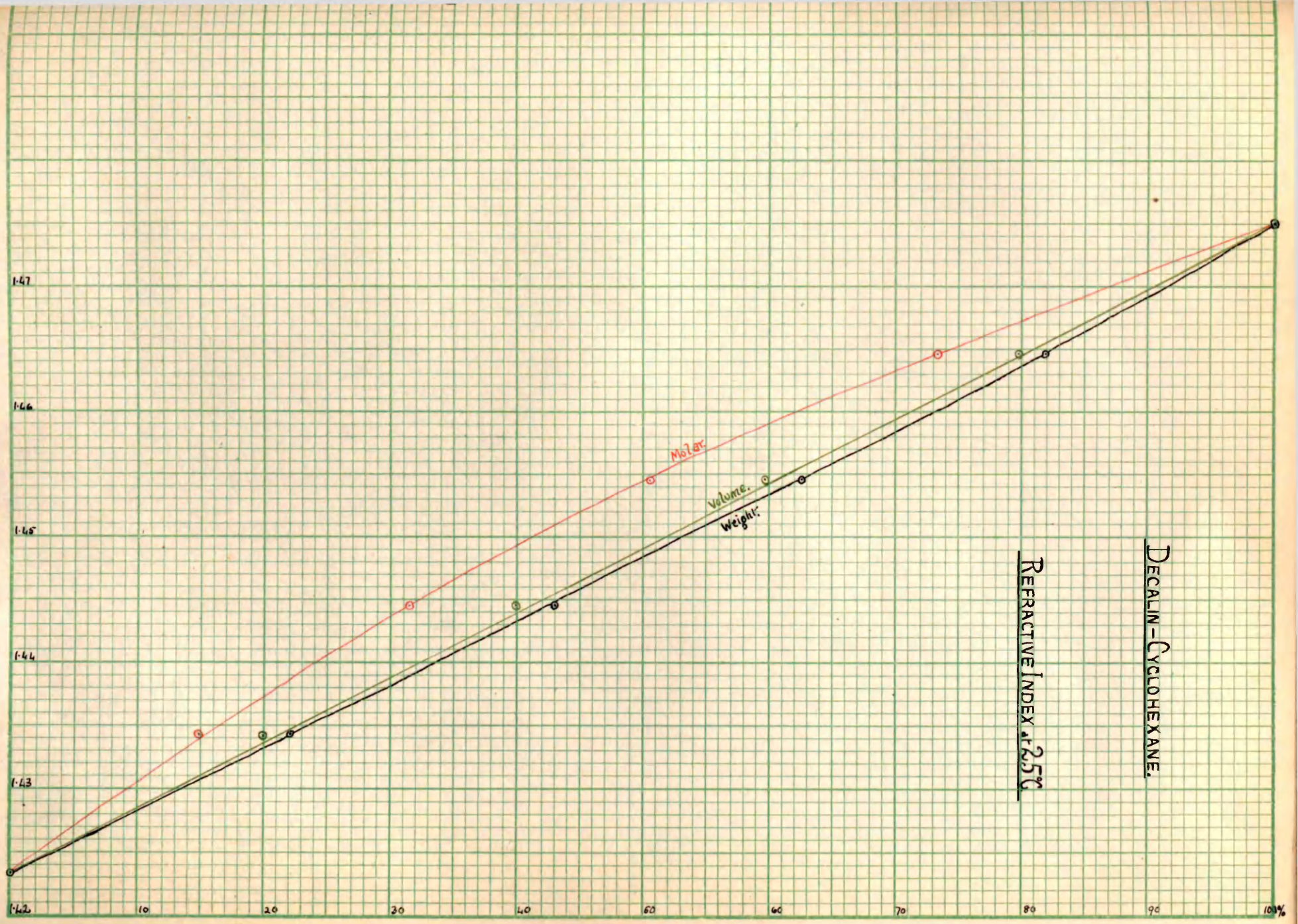

DECALIN–CYCLOHEXANE.
VISCOSITY at 25°C.
Molar.
Volume.
Weight.
220
210
190
170
150
130
110
100
90
100%
90
80
70
60
50
40
30
20
10
$C_{10}H_{18}$ %.
$\eta \times 10^5$ poises.

DECALIN–CYCLOHEXANE.

FLUIDITY at 25°C.

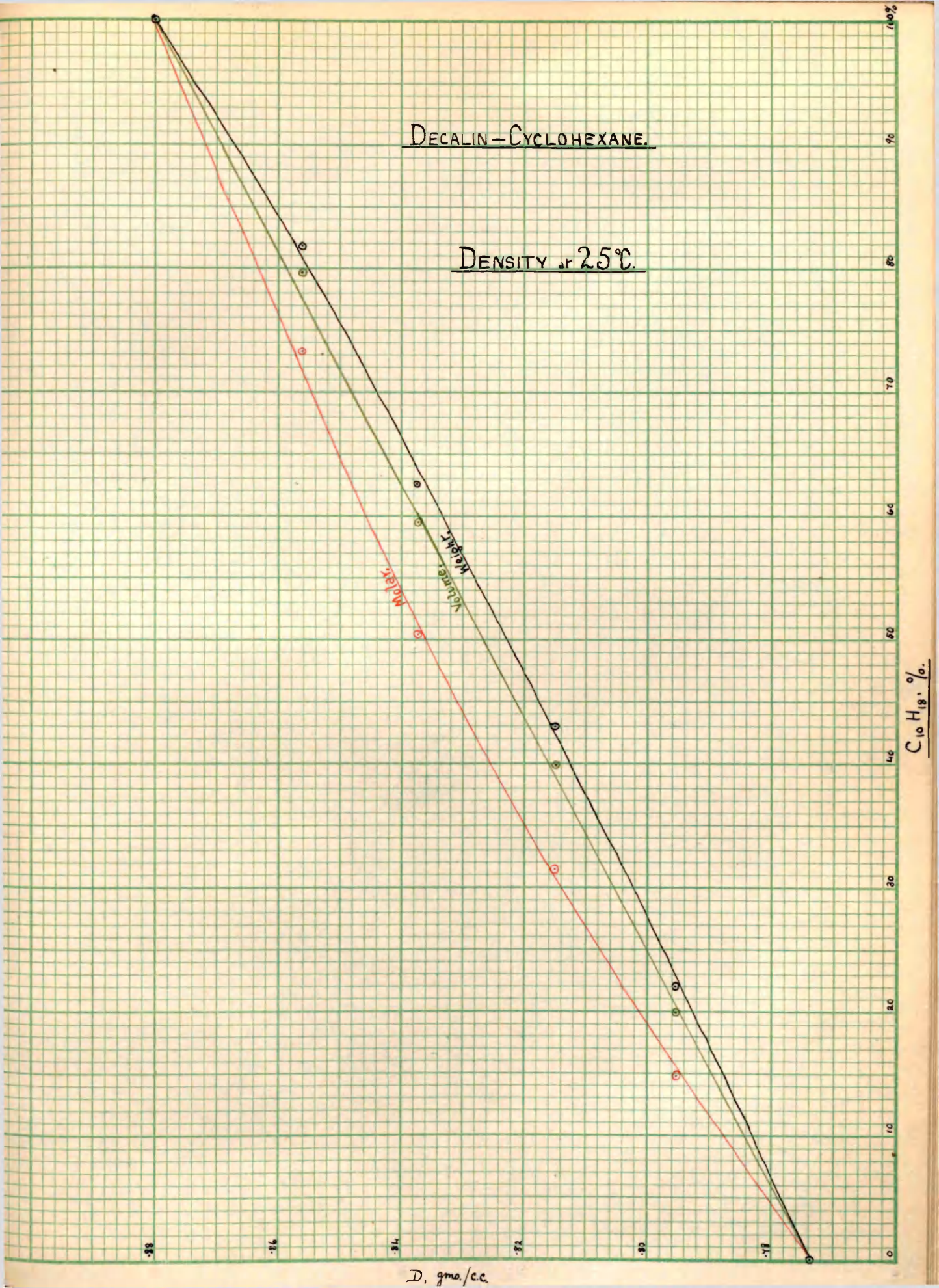


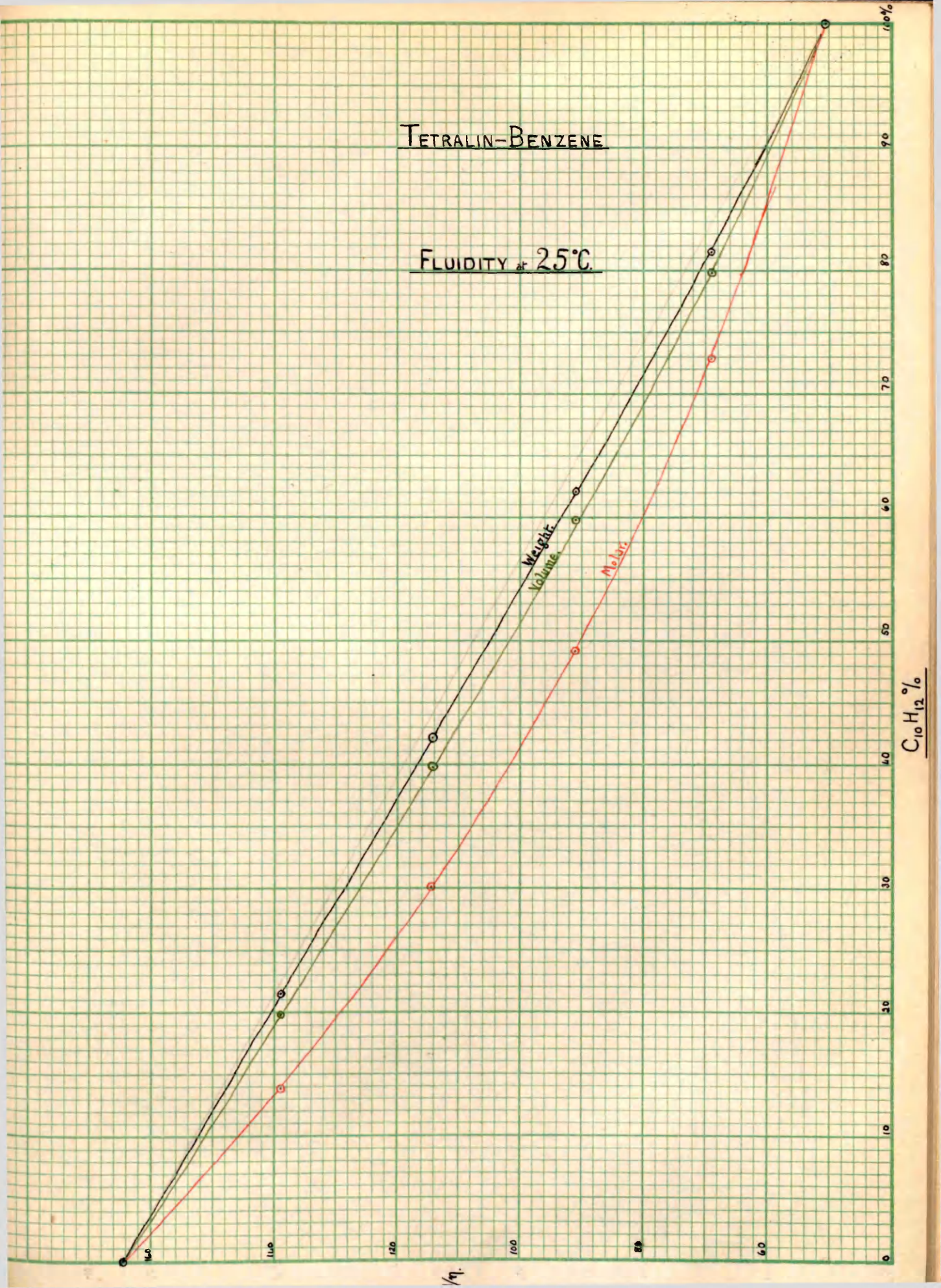

DECALIN—CYCLOHEXANE.
SURFACE TENSION at 25°C.
Weight.
Volume.
Molar.
30
29
28
27
26
25
24
γ. dynes/cm.
100%
90
80
70
60
50
40
30
20
10
0
$C_{10}H_{18}$ %.

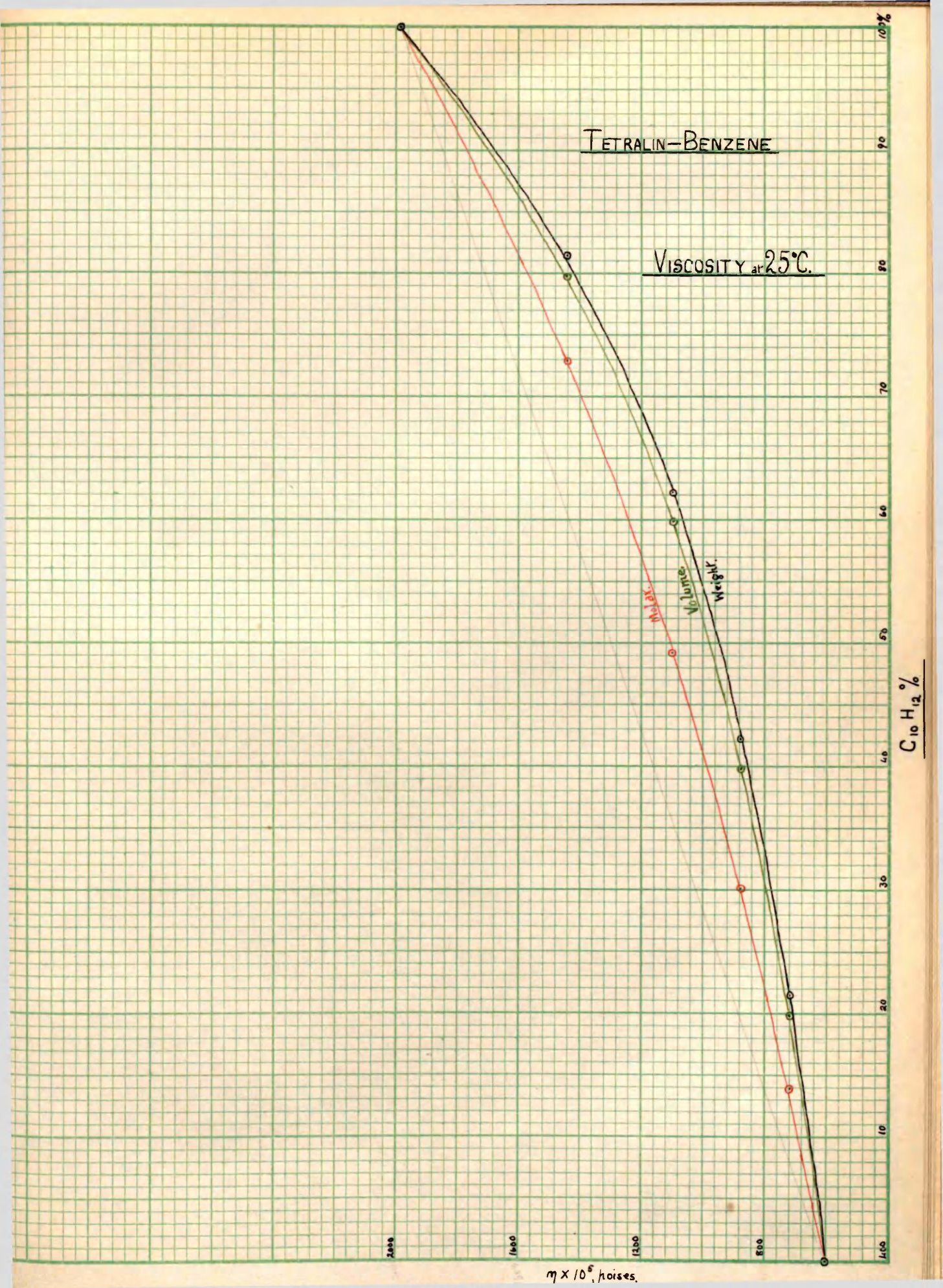


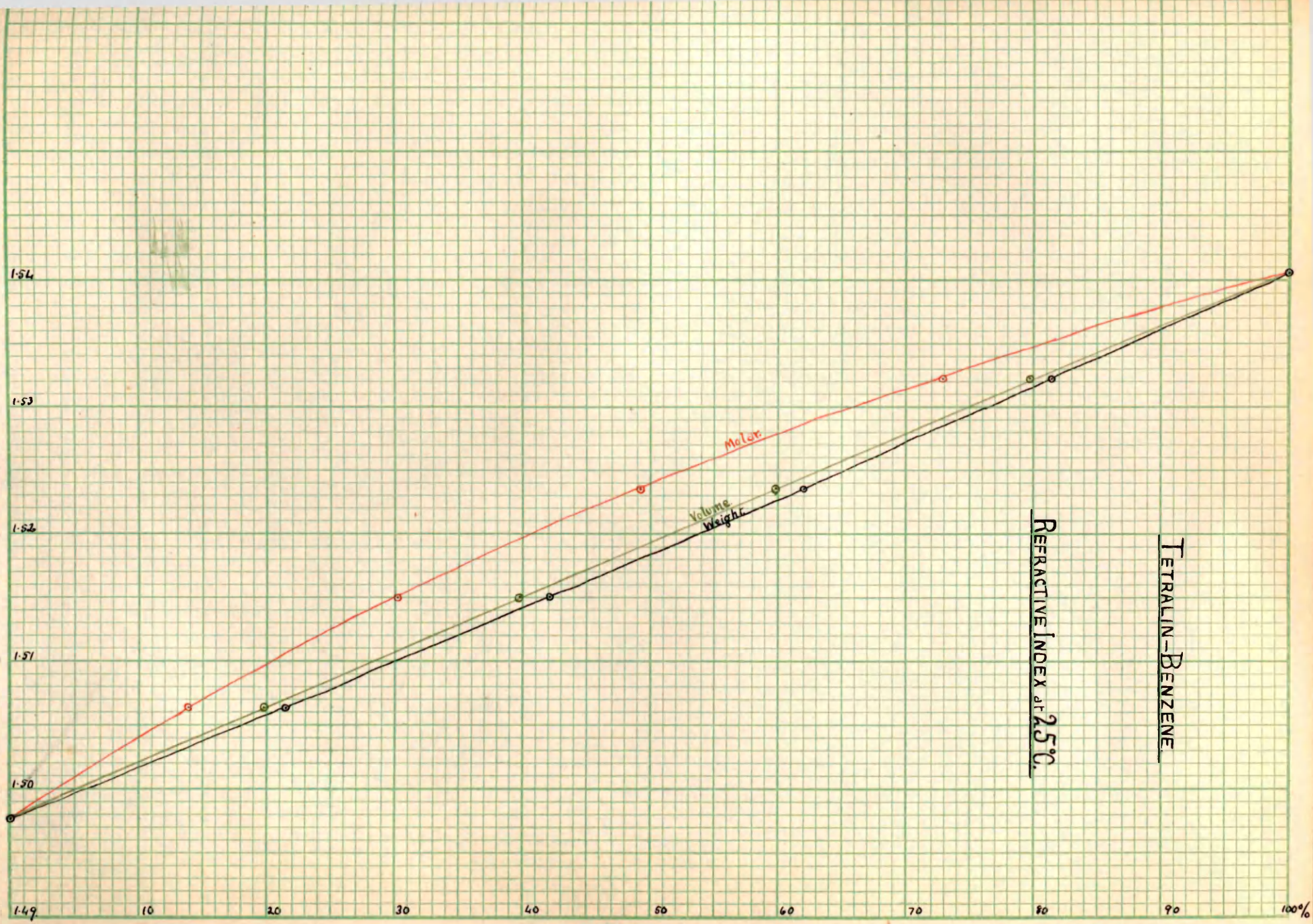
DECALIN–CYCLOHEXANE.

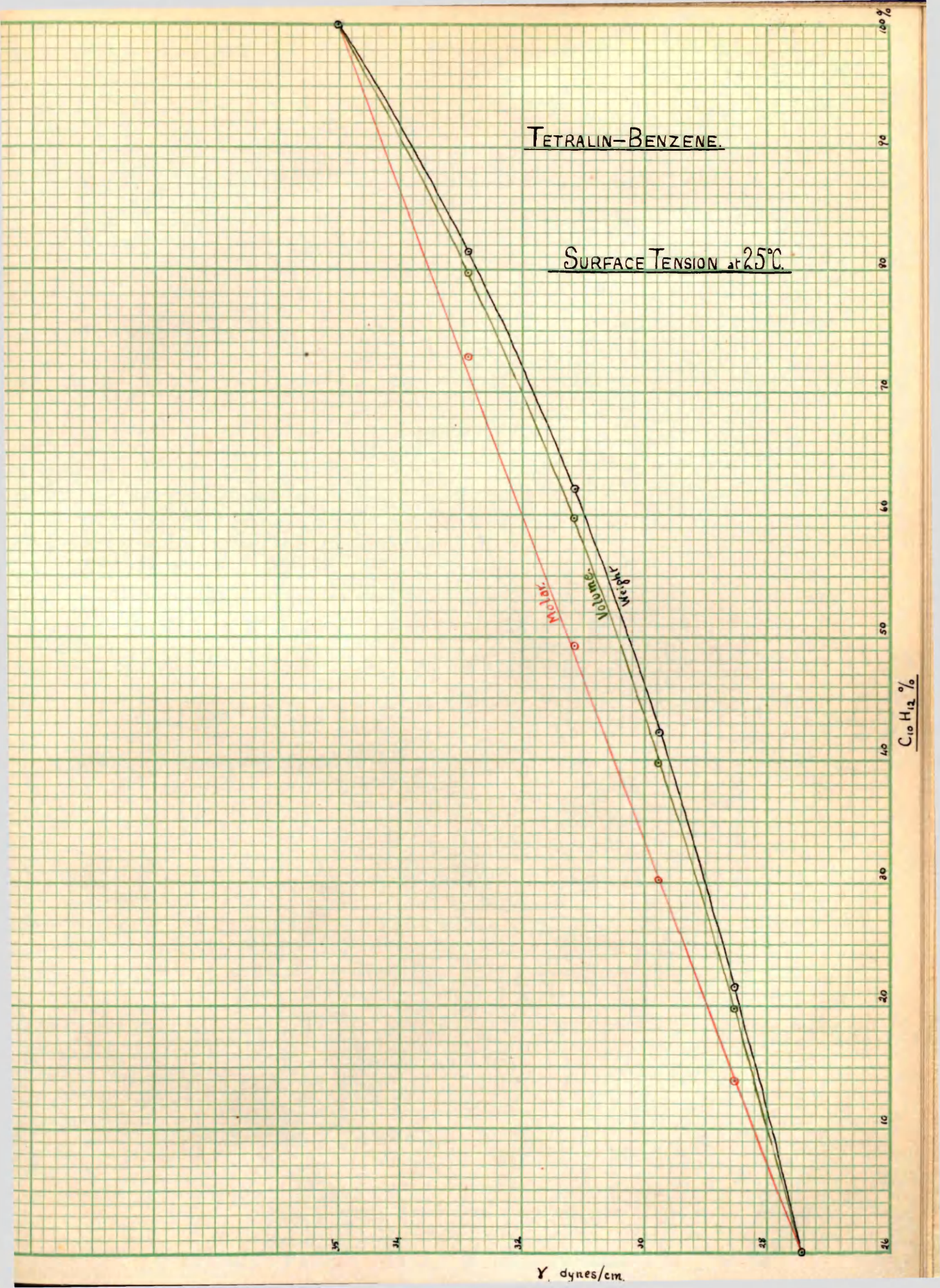
REFRACTIVE INDEX at 25°C.

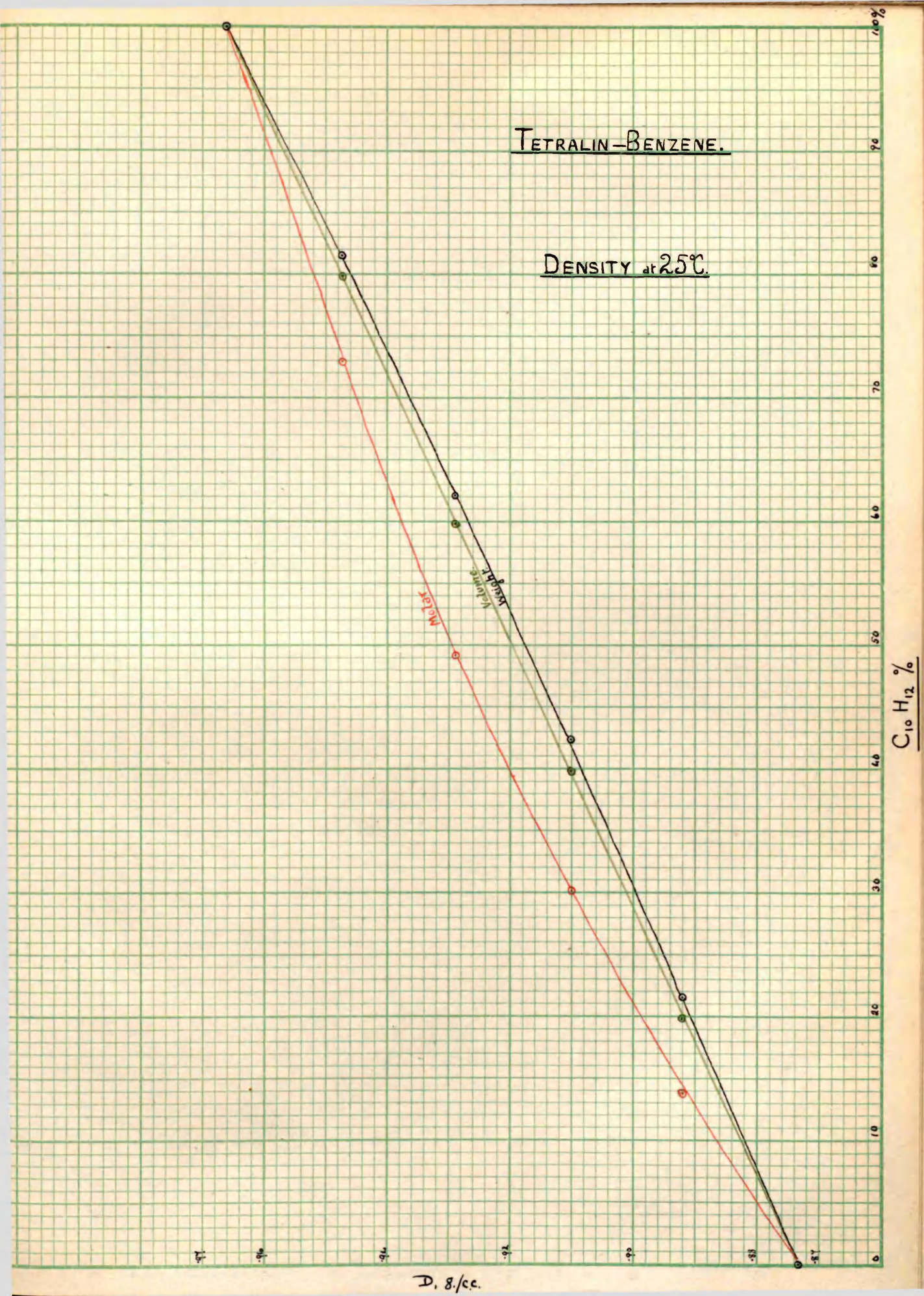

DECALIN—CYCLOHEXANE.
DENSITY at 25°C.
Molar.
Volume.
Weight.
D, gms./c.c.
C10H18, %.


TETRALIN-BENZENE
FLUIDITY at 25°C.
Weight
Volume
Molar
160
140
120
100
80
60
0
10%
90
80
70
60
50
40
30
20
10
0
C10H12 %
1/η.


TETRALIN–BENZENE
VISCOSITY at 25°C.
Molar.
Volume.
Weight.
100%
90
80
70
60
50
40
30
20
10
0
2000
1600
1200
800
400
$\eta \times 10^6$, poises.
$C_{10}H_{12}$ %

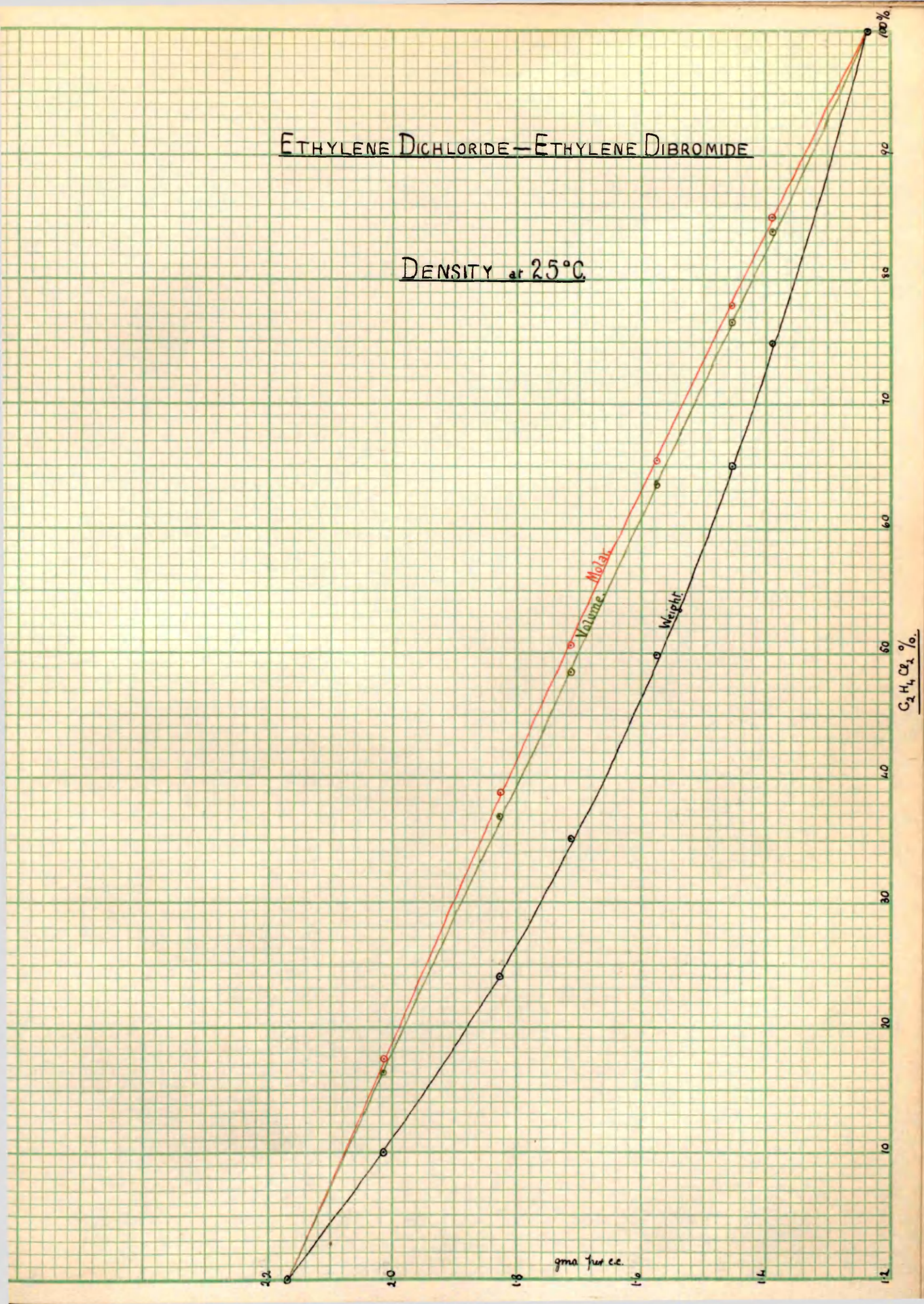

Tetralin–Benzene
Refractive Index at 25°C.
Molec.
Volume
Weight
1·54
1·53
1·52
1·51
1·50
1·49
10
20
30
40
50
60
70
80
90
100%
C10 H12 %


TETRALIN–BENZENE.
SURFACE TENSION at 25°C.
Weight
Volume
Molar.
100 %
90
80
70
60
50
40
30
20
10
0
36
34
32
30
28
26
γ dynes/cm.
C10 H12 %


TETRALIN–BENZENE.
DENSITY at 25°C.
Molar
Volume
Weight
100%
90
80
70
60
50
40
30
20
10
0
.98
.96
.94
.92
.90
.88
.86
D, g./cc.
C10 H12 %

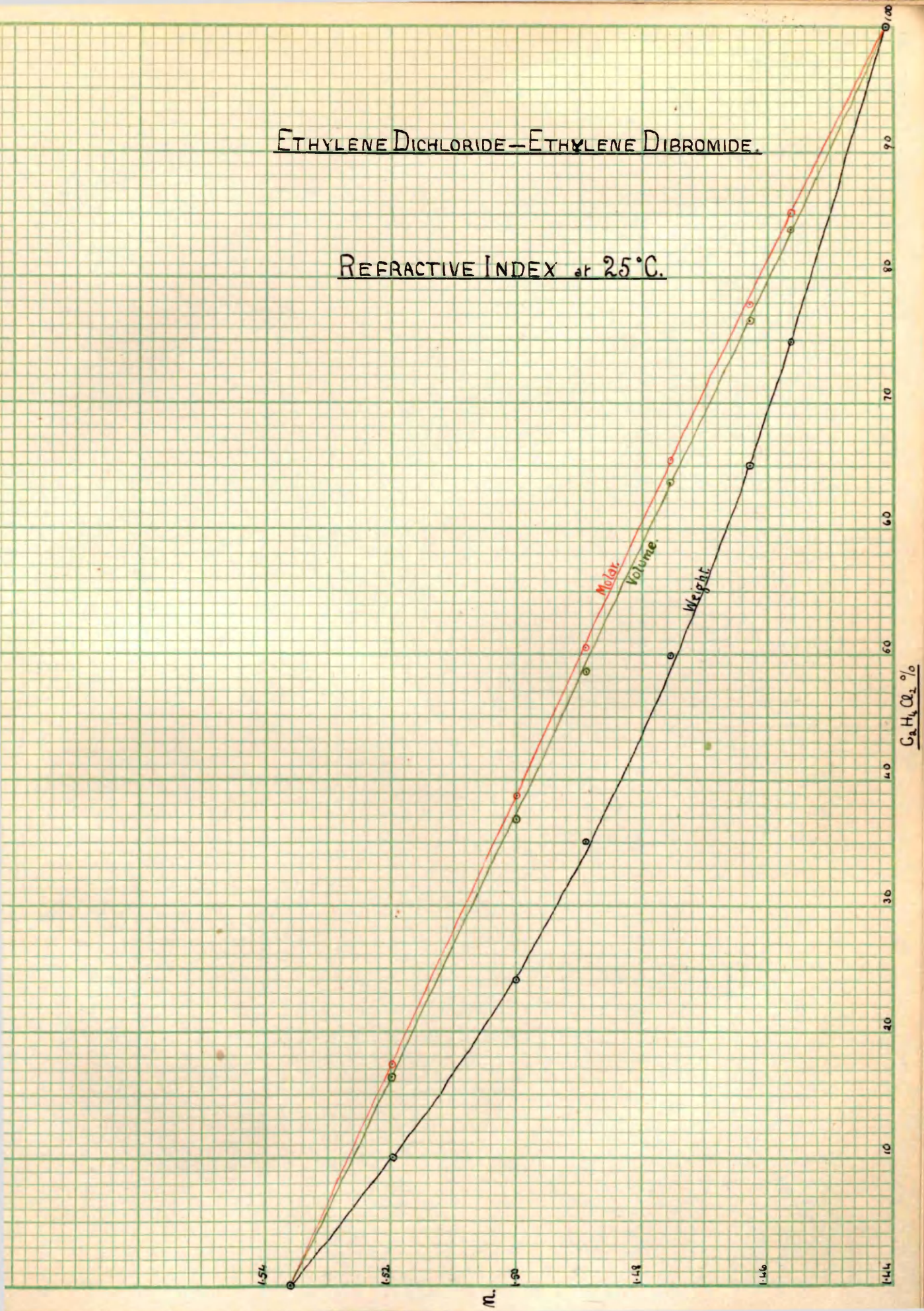
Ethylene Dichloride—Ethylene Dibromide

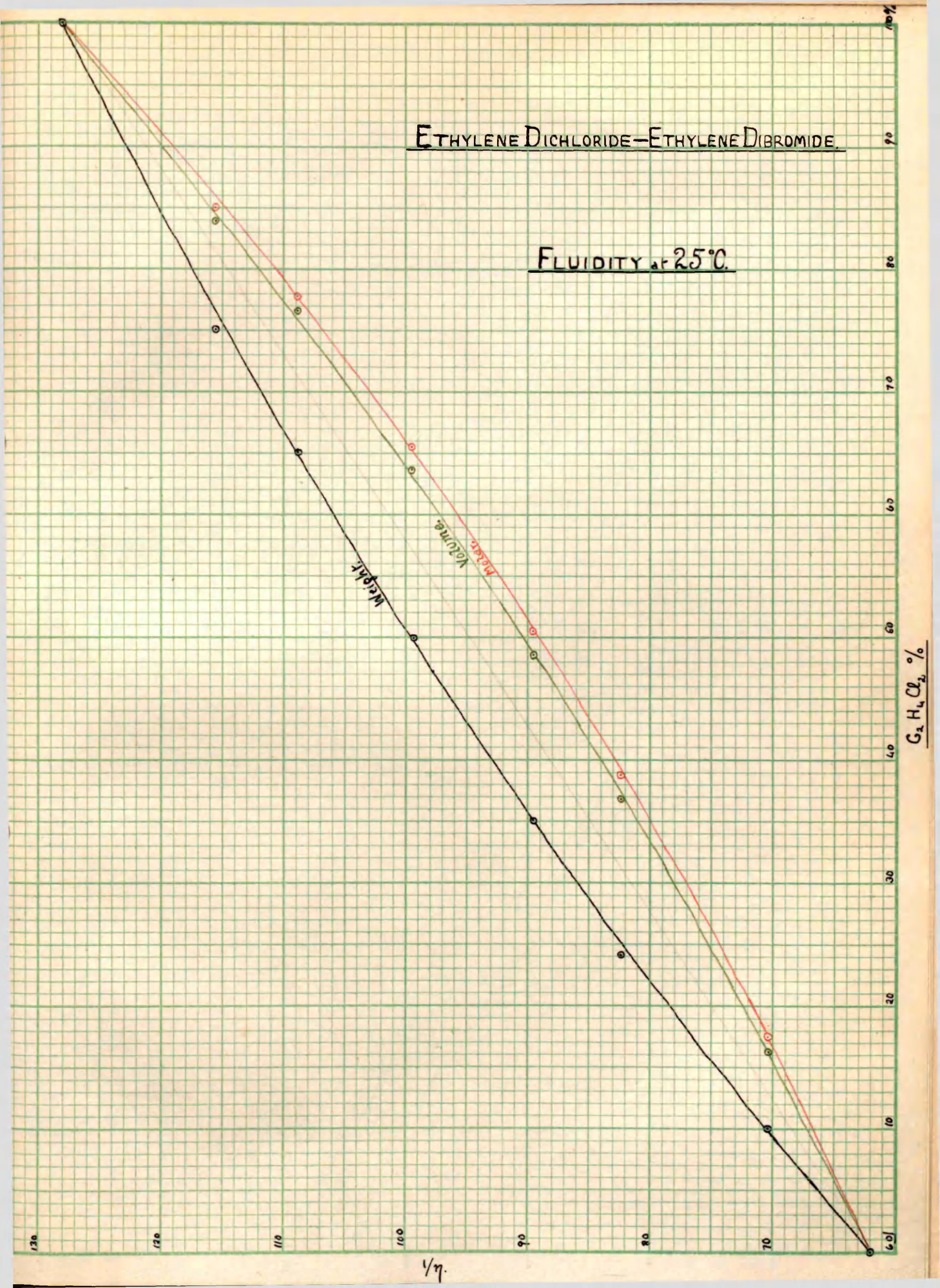
Density at 25°C.



Ethylene Dichloride—Ethylene Dibromide.

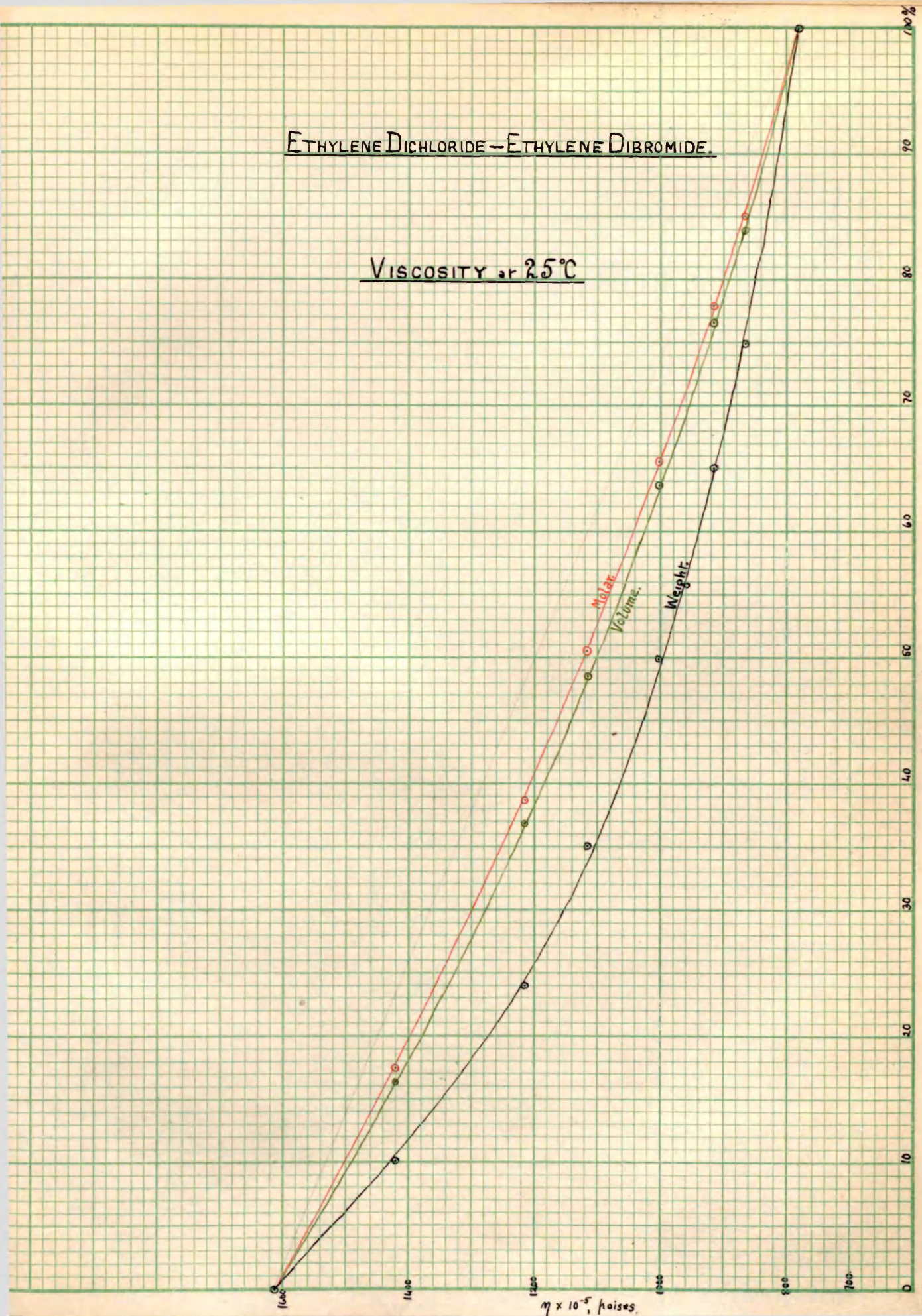
Refractive Index at 25°C.




Ethylene Dichloride—Ethylene Dibromide.
Fluidity at 25°C.
Molar.
Volume.
Weight.
$C_2H_4Cl_2$ %
1/η.

Ethylene Dichloride – Ethylene Dibromide.

Viscosity at 25°C



Ethylene Dichloride—Ethylene Dibromide.

Surface Tension at 25°C.